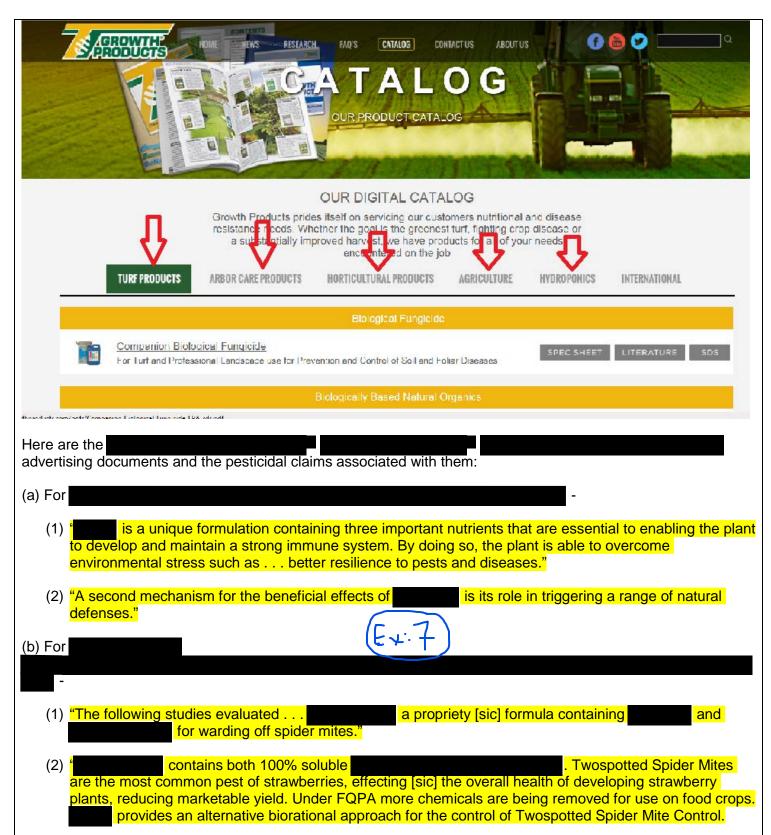
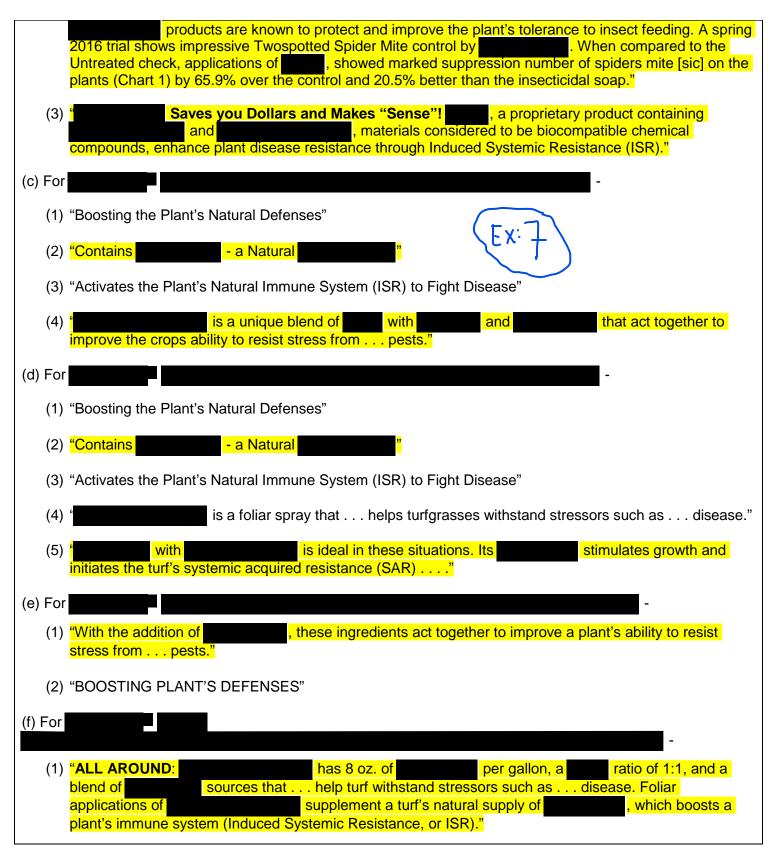
ENFORCEMENT CASE REVIEW				I. PRODUCT REGISTRATION STATUS				
				E	ECR Log No. 16-2-4			
Ex: 7 Product Label								
BRAND NAME(S):			ı		PANY AME:	Growth Pro	oducts	, Ltd. (Growth Products)
WEBSITE(S):	WEBSITE(S): www.growthproducts.com			Com Addr	PANY RESS:			
	В	asic R	Registr	atior	) Stat	us		
REGISTERED			<u></u>					
	DATE ACCEPT	ED:				FDΔ	REG. NO	)·
	REGISTRANT NAME AND ADDRESS:					LIA	KLO. IV	
UNREGISTER		<u> </u>						
	NO APPLICATION							
	APPLICATION PENDING		FILE SYM	IBOL:				
	CANCELLED/SUSPENDED		D	ATE:				
						EXISTING S	TOCK:	
		DEADLINE		S FOR:	DISTRIB	UTOR:		
							USER:	
	REGISTRANT REQUESTED							
	NONPAYMENT OF MAINTENANCE FEES							
	CANCELLATION / SUSPENSION	NC	ORDER	OF:				
	OTHER (please explain):							
□ EXEMPTED UNDER 40 CFR SECTION:								
	Distr	ibuto	r Regi	strat	ion S	tatus		
SUPPLEMENTAL REGISTRATION YES NO DATE OF SUPPLEMENTAL REGISTRATION: PRODUCT NAME:					PRODUCT NAME:			
DISTRIBUTOR NAME(S) AND ADDRESS(ES):								
Pertinent Registration Information								
NONE								
Pesticide / Device Status								
IS THIS A PESTICIDE? YES NO (40 CFR § 152.15)								
□ NO PESTICIDAL CLAIMS □ NO PESTICIDAL EFFECT				IS THIS A DEVICE? YES NO				

# Pest Control Claims and Other Factors That Identify the Product as a Pesticide or Device

(Including labeling and advertising) labels, as The attached to this enforcement case review (ECR) request, contain the following pesticidal claims: (a) From the label -(1) "Activates ISR (Induced Systemic Resistance)" is a unique formulation containing three important ingredients that are know [sic] to activate Induce [sic] Systemic Resistance (ISR) in plants. By doing so, the plant is able to . . . better resist insect and fungal attack." contains , a natural which produces a broad spectrum of resistance when a plant is exposed to fungi, bacteria and viruses." label -(b) From the (1) "Applications of early in the plant's life can encourage earlier development, increased growth (c) From the label -(1) "Helps Increase Resistance to Disease & Pests" contains which . . . increases the turf's resistance to disease and pests." (d) From the ' label -(1) "Increases Root Mass" (2) "Aids In Bloom Set" In addition, Growth Products' website (referenced on the labels attached to this ECR request) presents numerous pesticidal claims associated with , which appear in advertising documents directed to customers that are involved in caring for plants in different markets (e.g., turf, arbor care, and agriculture):





(g) For ———————————————————————————————————
is a good example of a product with this ratio and an excellent choice for an initial application of nutrients for rapid stimulation and development of the root system. This ideal ratio in combination with the an anatural plant phytohormone, found in will also bring strained plants out of stress and decline."
(h) For
(1) " is another product to use for strengthening a plant's roots and also its immune system with the powerful active metabolite ."
(i) For -
(1) reduces stress in seedlings. By providing the same active ingredient as in works on plants much the same way it works for humans – by boosting the plant's natural immune system in response to stress, through systemic acquired resistance or SAR."
(j) For
(1) "Increases Resistance to Disease & Pests"
(2) " increases the turf's resistance to disease and pests."
(k) For
(1) ' increases the turf's resistance to disease and pests"
(I) For '
(1) "Strengthens Plants [sic] Immune System"
(2) "Growth-Stimulating Effects"
(3) "Because of this unique property, are viewed as excellent initiator to improve the plant's resistance, by stimulation of natural host defenses against other stress."
(4) "At appropriate rates, can provide stimulation to plants to make a broad spectrum of biologically active metabolites, which does not occur with protection against stress conditions."
(5) "A pre-bloom foliar application will produce growth-stimulating properties increasing flower number fruit size"
Additionally, the labels and website advertising of claim that these products contain

Products' website and on the and and and and and all labels attached to this ECR request, Growth Products makes pesticidal claims in relation to these substances. All such pesticidal claims are .
Finally, several other products from Growth Products contain the substances listed in the previous paragraph.  The advertising materials for these products also contain pesticidal claims, some that are associated with the specific substances in
(a) For
(1) (2) "SAR (Systemic Acquired Resistance)"
(3) "Critical Signal Molecule for Plant Defenses"
(4) falls into the category of a plant has significant impact on plant growth and development, photosynthesis, transpiration, ion uptake and transport, and signals the plant's defense against pathogens."
(5) "Citrus and tomatoes sprayed with are known to have reduced damage from insects and pathogens."
(b) For
(1) "Increases Plant's Resistance to Disease"
which increases the plant's resistance."
(3) "A continuous source of is very important to enhance the plants' resistance to sucking insects and promotes the natural defense to fungal diseases."
(c) For
(1) "By the cell walls of plant tissue, and wards off fungal disease."
also increases the plant's resistance to disease and pests."
(d) For
(1) "Strengthens Plants [sic] Immune System"
(2) "Growth-Stimulating Effects"
(3) "Translocation in phloem allows  Because of this unique property, resistance, by stimulation of natural host defenses against other stress."

(4)	"At appropriate rates, can provide stimulation to plants to make a broad spectrum of biologically active metabolites, which does not occur with protection against stress conditions."
(5)	"A pre-bloom foliar application will produce growth-stimulating properties increasing flower number fruit size"
(e) Fo	-
(1)	"THE STRESS FIGHTER TRIGGERS THE PLANT'S DEFENSE SYSTEM"
(2)	"Improves disease-resistance in turf"
(f) For	
	) -
(1)	"Once inside a plant, it is extremely mobile and works to enhance root development, and improve crop resistance to disease."
(2)	"Applied at critical growth stages in a plant's life cycle, it ensures superior root formation, seedling growth, bud formation, blossom and fruit set. It boosts a plant's resistance to stress and disease."
(3)	"Increases Fruit Set and Development"
(4)	"With a plant's natural defense mechanisms are heightened so that diseases are more easily repelled. It is a phytoalexin, which attacks the disease directly. The production of polysaccharides strengthens the cell wall adding additional protection. The cells also send "alarm signals" to cells that have not yet been attacked."

ENFORCEMENT CASE REVIEW	II. CONCERNS
	ECR Log No. 16-2-4

# **Product Labeling**

BRAND NAME(S):	COMPANY NAME AND ADDRESS:
WEBSITE(S):	Growth Products, Ltd. (Growth Products) 80 Lafayette Avenue
www.growthproducts.com	White Plains, NY 10603



#### REVIEW

#### INFORMATION AND QUESTIONS SUBMITTED WITH THIS ECR REQUEST

EPA Region 2 has submitted an ECR request on four products:
. With this ECR request, EPA Region 2 provided labels for the products
and email correspondence between EPA Region 2, EPA Region 10, the Office of Pesticide Programs (OPP), and the
Washington State Department of Agriculture.
In its ECR request, EPA Region 2 asked OPP to answer the following questions:
(1) For - Are the claims in the fifth bullet (above), "overcome environmental stress" and "resist
insect and fungal attack," considered pesticidal? Does this product require EPA registration? Please explain.
(2) For
Does this require EPA registration? Please explain.
(2) For
(3) For a second bullet, "increases resistance," considered pesticidal?

Does this require EPA registration? Please explain.

(4) For - Do these descriptions make this product a plant growth regulator? Is the claim in the 4th bullet, "reduces summer stress," considered pesticidal? Does this require EPA registration? Please explain.

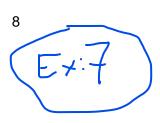
These questions are addressed in the "Pest Control Claims and Other Factors That Identify the Product as a Pesticide or Device" section above and in the analysis provided below.

#### **ANALYSIS**

In addition to nitrogen stabilizers and substances (or mixtures of substances) that are intended for preventing. destroying, repelling, or mitigating any pest, are also included within the pesticide definition under section 2(u) of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). In FIFRA § is defined as

According to 40 CFR § 152.15, the EPA considers a substance "to be intended for a pesticidal purpose, and thus to be a pesticide requiring registration, if:

- (a) The person who distributes or sells the substance claims, states, or implies (by labeling or otherwise):
  - (1) That the substance (either by itself or in combination with any other substance) can or should be used as a pesticide; or
  - (2) That the substance consists of or contains an active ingredient and that it can be used to manufacture a pesticide; or
- (b) The substance consists of or contains one or more active ingredients and has no significant commercially valuable use as distributed or sold other than (1) use for pesticidal purpose (by itself or in combination with any other substance), (2) use for manufacture of a pesticide; or



(c) The person who distributes or sells the substance has actual or constructive knowledge that the substance will be used, or is intended to be used, for a pesticidal purpose."

This regulation describes two tests for identifying whether a substance is a pesticide: (1) a pesticidal claims test (subpart (a) above) and (2) a pesticidal use test (subparts (b) and (c) above).

To be considered "intended for a pesticidal purpose" by the EPA, a substance needs to meet only one of the two tests.1

#### a) Pesticidal Claims Test

substance can or should be used as a pesticide and/or that a substance contains an active ingredient and can be used to produce a pesticide. Growth Products announces the intended pesticidal use of to the public/potential consumers by making explicit pesticidal claims on the labels of the products and on its website (referenced on the product labels; see U.	ì
to the public/potential consumers by making	
explicit posticidal claims on the labels of the products and on its website (referenced on the product labels; see 11)	_
explicit pesticidal cialins on the labels of the products and on its website (referenced on the product labels, see o	S.
EPA (2008)); some of these are unique pesticidal claims (e.g., resistance to disease) that are typical of a systemic	;
acquired resistance (SAR) and induced systemic resistance (ISR) inducers, such as (U.S. EPA 2012	,
USDA - ARS 2003). Additionally, Growth Products sells other products that contain some of the same substances	in :
and makes pestic	
claims for these products on its website. See the "Pest Control Claims and Other Factors That Identify the Product	t as
a Pesticide or Device" section for more details.	

claims test; therefore, the EPA considers these products

the pesticidal

for a pesticidal purpose.

#### b) Pesticidal Use Test

The pesticidal use test involves determining whether a product contains one or more active ingredients and has no significant commercially valuable use as distributed or sold other than use for pesticidal purposes or for manufacture of a pesticide and/or whether the seller or distributor has actual or constructive knowledge<sup>2</sup> that the substance will be used, or is intended to be used, for a pesticidal purpose.<sup>3</sup> If a product meets either or both portions of this test,

9

<sup>&</sup>lt;sup>1</sup> See page 37917 of the preamble to the September 26, 1984, Proposed Rule for "Pesticide Registration and Classification" Procedures" that states the following: "Section 152.15 would describe the circumstances under which the Agency will presume that a substance is being distributed and sold with the intent that it be used as a pesticide. Clearly, either expressed or implied claims or representations by the seller, such as labeling or advertising, would be evidence of intent. However, the Agency believes that, in the absence of claims, a product may be considered to be a pesticide if the seller or distributor is aware of the intended uses of the product as a pesticide. This may be the case either because there are no other significant uses of the product, or because other circumstances of the sale and distribution are such that he should reasonably know the ultimate use of the product as a pesticide." (Federal Register, 1984).

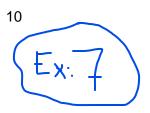
<sup>&</sup>lt;sup>2</sup> Criteria that the EPA considers in determining actual or constructive knowledge include things like promotional claims and advertising and common knowledge of the general business of the person to whom the substance is sold (Federal Register, 1988).

<sup>3</sup> According to Federal Register (1988), the pesticidal use test (i.e., 40 CFR § 152.15(b) and 40 CFR § 152.15(c)) was "intended to address longstanding enforcement problems in which neither labeling nor advertising clearly states or implies that the product is a pesticide, but the product is sold under circumstances in which it is clear that the product is intended for a pesticidal purpose."

the EPA will identify it as a pesticide.

To determine whether contain active ingredients and have no significant commercially valuable uses other than pesticidal, which is the first part of the pesticidal use test, the EPA examined the composition, claims, and use directions of the products.
Growth Products' website. According to public literature, these substances act directly on and/or indirectly through stimulation of plant defense responses to certain fungal pathogens) and cannot be used directly by plants as a yamakawa, 2009). The ability of ability of and and is further supported by a search in the Office of Pesticide Programs' Information Network (OPPIN); this search yielded a listing of 49 pesticide products, all of which are considered to be or for manufacturing products (U.S. EPA, 2017a and 2000). Given the information above and how the products are applied, the EPA is not aware of any significant commercially valuable uses other than pesticidal for in the subject products.
, based on information from their labels and/or presented on Growth Products' website. Regarding this component, there are as an active ingredient (U.S. EPA, 2017b and 2007). This particular substance can also be used as a (National Organic Standards Board Technical Advisory Panel, 2003), so an argument could likely be made, as long as the uses and claims described for the products align with the aforementioned non-pesticidal use (e.g., applications are made to the soil to improve its characteristics, like pH and porosity, for plant growth), that it has significant commercially valuable uses outside of the pesticidal realm.
, based on information from their labels and/or presented on Growth Products' website.  (Davies, 2010; Raskin, 1992), and there are as an active ingredient (U.S. EPA, 2017c and 2012). Companies with products that contain nutrients could possibly argue that the commercially valuable use other than pesticidal). In this case, however, the products do not appear to contain the nutrients that one would expect to be information above and how the products are applied, the EPA is not aware of any significant commercially valuable uses other than pesticidal for in the subject products.
- One product contains based on information from its label and presented on Growth Products' website.  (Nardi et al., 2002; U.S. EPA, Undated(i) and 2014), and there  as an active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a active ingredient (U.S. EPA, 2017d). This particular substance can also be used as a control of the products align with the aforementioned non-pesticidal use (e.g., applications are made to the soil to improve its characteristics, like pH and porosity, for plant growth), that it has significant commercially valuable uses outside of the pesticidal realm.

<sup>5</sup> See Liu *et al.* (2015) for more information on



for the composition and intended uses of the only exclusion that could possibly apply is found under 40 CFR §

In this case, however, there is not enough information to determine whether these products qualify for this exclusion. To meet the first criterion in 40 CFR §

The only exclusion that could possibly apply is found under 40 CFR §

In this case, however, there is not enough information to determine whether these products qualify for this exclusion. To meet the products with the products would need to provide data and/or other information to the EPA to show that its products meet the presenting complete toxicological and irritation information for the products). Growth Products would also need to add text to the product labels, explicitly specifying that the products are not to be used on the product consist only of the control of the products consist only of the products contain the products of the products contain the products are not fall under any of the substance types listed.)

REVIEWER (NAME AND PROGRAM OFFICE) / SIGNATURE:	CONCURRING SUPERVISOR (NAME AND PROGRAM OFFICE) / SIGNATURE:			
	Land Sch			
Jeannine Kausch, Product Manager 92 Microbial Pesticides Branch Biopesticides & Pollution Prevention Division (7511P) Office of Pesticide Programs	Linda A. Hollis, Chief Biochemical Pesticides Branch Biopesticides & Pollution Prevention Division (7511P) Office of Pesticide Programs			
DATE: 10/06/2017	DATE: 10/0/07			

#### **References and Attachments**

Davies PJ (ed.). 2010. The Plant Hormones: Their Nature, Occurrence, and Functions, pp 1–15. In: *Plant Hormones – Biosynthesis, Signal Transduction, Action! (Revised Third Edition)*. Springer, New York, New York.

Federal Register. 1988. Pesticide Registration Procedures; Pesticide Data Requirements (53 FR 15952) (May 4, 1988). Available from <a href="http://www.heinonline.org/HOL/Index?collection=fedreg">http://www.heinonline.org/HOL/Index?collection=fedreg</a>.

Federal Register. 1984. Pesticide Registration and Classification Procedures (49 FR 37916) (September 26, 1984). Available from <a href="http://www.heinonline.org/HOL/Index?collection=fedreg">http://www.heinonline.org/HOL/Index?collection=fedreg</a>.

Liu G, Hanlon E, Li Y. 2015. Understanding and Applying Chelated Fertilizers Effectively Based on Soil pH (Publication #HS1208). Available from <a href="http://edis.ifas.ufl.edu/hs1208">http://edis.ifas.ufl.edu/hs1208</a>.

Nardi S, Pizzeghello D, Muscolo A, Vianello A. 2002. Physiological effects of humic substances on higher plants. Soil Biology & Biochemistry 34:1527–1536. Available from http://www.humateproducts.com/images/Physiological effects of humic substances on higher plants.pdf.

National Organic Standards Board Technical Advisory Panel. 2003. Potassium silicate for use in crop production. Available from

https://www.ams.usda.gov/sites/default/files/media/Pot%20sil%20technical%20advisory%20panel%20report%202003.pdf.

Raskin I. 1992. Salicylate, a new plant hormone. Plant Physiology 99:799–803. Available from <a href="https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1080546/pdf/plntphys00707-0017.pdf">https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1080546/pdf/plntphys00707-0017.pdf</a>.

Rhode Island Golf Course Superintendents Association (RIGCSA). 2013. Phosphorous vs. Phosphite in Surf 'n' Turf (Dated September/October 2013).

Thao HTB, Yamakawa T. 2009. Phosphite (phosphorous acid): Fungicide, fertilizer or bio-stimulator? *Soil Science and Plant Nutrition* 55:228–234. Available from <a href="http://www.tandfonline.com/doi/pdf/10.1111/j.1747-0765.2009.00365.x">http://www.tandfonline.com/doi/pdf/10.1111/j.1747-0765.2009.00365.x</a>.

Traunfeld J, Nibali E. 2013. Soil Amendments and Fertilizers – Fertilizing Guidelines Included by Plant Group. Available from

https://extension.umd.edu//sites/extension.umd.edu/files/\_images/programs/hgic/Publications/HG42\_Soil\_Amendments and Fertilizers.pdf.

United States Department of Agriculture (USDA) – Agricultural Research Service (ARS). 2003. Helping Plants Defend Themselves, pp. 8–10. In: *Agricultural Research Magazine*. Available from <a href="http://www.ars.usda.gov/is/AR/archive/dec03/plant1203.pdf">http://www.ars.usda.gov/is/AR/archive/dec03/plant1203.pdf</a>.

U.S. EPA. Undated(i). Complex Polymeric Polyhydroxy Acids (CPPA) Biopesticides Registration Action Document. Available from <a href="http://www.regulations.gov">http://www.regulations.gov</a> (search for "EPA-HQ-OPP-2009-0917-0008").

U.S. EPA. 2017a. Summary Report of Active Registrations That Contain Phosphorous Acid (PC Code: 076002, CAS No.: 10294-56-1) or Mono- and Di-Potassium Salts of Phosphorous Acid (PC Code: 076416, CAS No.: 13492-26-7).

- U.S. EPA. 2017b. Summary Report of Active Registrations That Contain Potassium Silicate (PC Code: 072606, CAS No.: 1312-76-1).
- U.S. EPA. 2017c. Summary Report of Active Registrations That Contain Salicylic Acid (PC Code: 076602, CAS No.: 69-72-2).
- U.S. EPA. 2017d. Summary Report of Active Registrations That Contain Complex Polymeric Polyhydroxy Acids (PC Code: 078503, CAS No.: N/A) or Humates (PC Code: 021818, CAS No.: N/A).
- U.S. EPA. 2014. Humates (Humic Acid; Humic Acids, Potassium Salts; Humic Acids, Sodium Salts; and Humates Derived from Leonardite) Biopesticides Registration Action Document (Last Updated March 13, 2014). Available from <a href="http://www.regulations.gov">http://www.regulations.gov</a> (search for "EPA-HQ-OPP-2012-0251-0003").
- U.S. EPA. 2012. Salicylic Acid Biopesticides Registration Action Document (Dated January 10, 2012). Available from <a href="http://www.regulations.gov">http://www.regulations.gov</a> (search for "EPA-HQ-OPP-2011-0009-0003").
- U.S. EPA. 2008. Labeling Committee Projects/Labeling Committee Statements of Interest to General Public Web Site Addresses on Pesticide Product Labeling (Dated October 14, 2008). Available from <a href="https://archive.epa.gov/pesticides/regulating/con-labels/web/pdf/weblabeling.pdf">https://archive.epa.gov/pesticides/regulating/con-labels/web/pdf/weblabeling.pdf</a>.
- U.S. EPA. 2007. Potassium Silicate Biopesticides Registration Action Document (Dated September 7, 2007). Available from <a href="https://www3.epa.gov/pesticides/chem-search/reg-actions/registration/decision-PC-072606-7-Oct-07.pdf">https://www3.epa.gov/pesticides/chem-search/reg-actions/registration/decision-PC-072606-7-Oct-07.pdf</a>.
- U.S. EPA. 2000. Phosphorous Acid and Its Ammonium, Sodium, and Potassium Salts (076002) [and] Mono- and Di-Potassium Salts of Phosphorous Acid (076416) Fact Sheet (Dated April 2000). Available from <a href="https://www3.epa.gov/pesticides/chem\_search/reg\_actions/registration/fs\_G-133\_04-April-00.pdf">https://www3.epa.gov/pesticides/chem\_search/reg\_actions/registration/fs\_G-133\_04-April-00.pdf</a>.

# A. INTRODUCTION

# A1. The Plant Hormones: Their Nature, Occurrence, and Functions

#### Peter J. Davies

Department of Plant Biology, Cornell University, Ithaca, New York 14853, USA. E-mail: pjd2@cornell.edu

#### INTRODUCTION

## The Meaning of a Plant Hormone

Plant hormones are a group of naturally occurring, organic substances which influence physiological processes at low concentrations. The processes influenced consist mainly of growth, differentiation and development, though other processes, such as stomatal movement, may also be affected. Plant hormones<sup>1</sup> have also been referred to as 'phytohormones' though this term is infrequently used.

In their book *Phytohormones* Went and Thimann (10) in 1937 define a hormone as a substance which is transferred from one part of an organism to another. Its original use in plant physiology was derived from the mammalian concept of a hormone. This involves a localized site of synthesis, transport in the bloodstream to a target tissue, and the control of a physiological response in the target tissue via the concentration of the hormone. Auxin, the first-identified plant hormone, produces a growth response at a distance from its site of synthesis, and thus fits the definition of a *transported* chemical messenger. However this was before the full range of what we now consider plant hormones was known. It is now clear that plant hormones do not fulfill the requirements of a hormone in the mammalian sense. The synthesis of plant hormones may be localized (as occurs for animal hormones), but it may also occur in a wide range of tissues, or cells within tissues. While they may be transported and have their action at a distance this is not always the case. At one extreme we find the transport of

\_

<sup>1</sup> The following abbreviations are used throughout this book with no further definition: ABA, abscisic acid; BR, brassinosteroid; CK, cytokinin; GA gibberellin; IAA, indole-3-acetic acid

cytokinins from roots to leaves where they prevent senescence and maintain metabolic activity, while at the other extreme the production of the gas ethylene may bring about changes within the same tissue, or within the same cell, where it is synthesized. Thus, transport is not an essential property of a plant hormone.

The term 'hormone' was first used in medicine about 100 years ago for a stimulatory factor, though it has come to mean a transported chemical message. The word in fact comes from the Greek, where its meaning is 'to stimulate' or 'to set in motion'. Thus the origin of word itself does not require the notion of transport *per se*, and the above definition of a plant hormone is much closer to the meaning of the Greek origin of the word than is the current meaning of hormone used in the context of animal physiology.

Plant hormones<sup>2</sup> are a unique set of compounds, with unique metabolism and properties, that form the subject of this book. Their only universal characteristics are that they are natural compounds in plants with an ability to affect physiological processes at concentrations far below those where either nutrients or vitamins would affect these processes.

# THE DISCOVERY, IDENTIFICATION AND QUANTITATION OF PLANT HORMONES.

#### The Development of the Plant Hormone Concept and Early Work.

The plant hormone concept probably derives from observations of morphogenic and developmental correlations by Sachs between 1880 and 1893. He suggested that "Morphological differences between plant organs are due to differences in their material composition" and postulated the existence of root-forming, flower forming and other substances that move in different directions through the plant (10).

At about the same time Darwin (3) was making his original observations on the phototropism of grass coleoptiles that led him to postulate the existence of a signal that was transported from the tip of the coleoptile to the bending regions lower down. After further characterizations by several workers of the way in which the signal was moved, Went in the Netherlands was finally able to isolate the chemical by diffusion from coleoptile tips into agar blocks, which, when replaced on the tips of decapitated coleoptiles, resulted in the stimulation of the growth of the decapitated coleoptiles, and their bending when placed asymmetrically on these tips. This thus demonstrated the existence of a growth promoting chemical that was

\_

<sup>&</sup>lt;sup>2</sup> The term "plant growth substance" is also used for plant hormones but this is a rather vague term and does not describe fully what these natural regulators do - growth is only one of the many processes influenced. The international society for the study of plant hormones is named the "International Plant Growth Substance Association" (IPGSA). While the term plant growth regulator is a little more precise this term has been mainly used by the agrichemical industry to denote synthetic plant growth regulators as distinct from endogenous growth regulators.

synthesized in the coleoptile tips, moved basipetally, and when distributed asymmetrically resulted in a bending of the coleoptile away from the side with the higher concentration. This substance was originally named *Wuchsstoff* by Went, and later this was changed to *auxin*. After some false identifications the material was finally identified as the simple compound indoleacetic acid, universally known as IAA (11).

## **Discovery of Other Hormones**

Other lines of investigation led to the discovery of the other hormones: research in plant pathogenesis led to gibberellins (GA); efforts to culture tissues led to cytokinins (CK); the control of abscission and dormancy led to abscisic acid (ABA); and the effects of illuminating gas and smoke led to These accounts are told in virtually every elementary plant physiology textbook, and further elaborated in either personal accounts (9, 11) or advanced treatises devoted to individual hormones (see book list at the end of the chapter) so that they need not be repeated here. More recently other compounds, namely brassinosteroids (Chapters B7 and D7), jasmonates (Chapter F1) (including tuberonic acid, Chapter E5), salicylic acid (Chapter F2), and the peptides (Chapter F3) have been added to the list of plant hormones, and these are fully covered in this book for the first time. Polyamines, which are essential compounds for all life forms and important in DNA structure, have also been categorized as plant hormones as they can modulate growth and development, though typically their levels are higher than the other plant hormones. However, as little further understanding of their exact function in plants at the cellular and molecular levels has been added in the last few years, no individual chapter has been devoted to polyamines in this edition (a chapter on polyamines can be found in the previous edition (4): 2E Chapter C1).

It is interesting to note that, of all the original established group of plant hormones, only the chemical identification of abscisic acid was made from higher plant tissue. The original identification of the others came from extracts that produced hormone-like effects in plants: auxin from urine and the fungal cultures of *Rhizopus*, gibberellins from culture filtrates of the fungus Gibberella, cytokinins from autoclaved herring sperm DNA, and ethylene from illuminating gas. Today we have at our disposal methods of purification (such as high performance liquid chromatography: HPLC, following solid phase extraction: SPE cartridges) and characterization (gas chromatography-mass spectrometry: GC-MS, and high performance liquid chromatography-mass spectrometry: HPLC-MS) that can operate at levels undreamed of by early investigators (Chapter G1). Thus while early purifications from plant material utilized tens or even hundreds of kilograms of tissues, modern analyses can be performed on a few milligrams of tissue, making the characterization of hormone levels in individual leaves, buds, or even from tissues within the organs much more feasible. Thus it is not surprising to see the more-recently discovered hormones being originally

identified within plant tissues. Nonetheless only brassinosteroids were identified following investigations of plant growth effects, with the discovery of jasmonates, salicylic acid and peptide hormones deriving from work on insect and disease resistance.

Immunoassay (see 2<sup>nd</sup> edition, Chapter F2) is also used for hormone quantitation, though is considered much less precise because of interfering effects of other compounds and cross reactivity. Immunoassay columns can, however, permit the very precise isolation of plant hormones prior to more rigorous physico-chemical characterization. While the exact level and location of the hormones within the individual tissues and cells is still largely elusive (Chapter G1), huge strides have been made in analyzing and localizing the expression of genes for hormone biosynthesis using sensitive techniques such as PCR (polymerase chain reaction), or the expression, in transgenic plants, of marker genes driven by promoters of one or more steps in the biosynthetic process. The location of hormone action in tissues and cells has also been investigated by examining the location of marker gene expression driven by promoters of genes known to be induced by the presence of hormone (e.g. Chapter A2).

# THE NATURE, OCCURRENCE, AND EFFECTS OF THE PLANT HORMONES

Before we become involved in the various subsequent chapters covering aspects of hormone biochemistry and action it is necessary to review what hormones do. In subsequent chapters some or most of these effects will be described in more detail, whereas others will not be referred to again. It is impossible to give detailed coverage of every hormonal effect, and the reader is referred to the book list at the end of this chapter. The choice of topics for subsequent chapters has been determined largely by whether there is active research in progress in that area. Over the last few years there has been active progress in elucidating the biosynthesis, signal transduction and action of almost every hormone. Thus whereas previously the progress in understanding the action of one hormone was much better than that of another we now find increased understanding of hormone action across the board. A good case in point is cytokinin, where we now know much more about perception, signal transduction (Chapter D3) and action (Chapter C3) than just a few years ago. In fact progress on understanding one hormone as opposed to another has been leapfrogging: whereas the action of auxin at the physiological level was one of the first to be understood (Chapter C1) we still do not understand the connection between auxin signal transduction (Chapter D1) and its final action in inducing cell elongation, and while the identification of the auxin receptor was previously regarded as established, this is now regarded as far less certain. By contrast, after two decades of relatively little advance in the understanding of brassinosteroids, or even much interest in these compounds, following their discovery by extraction from *Brassica* pollen and the demonstration of growth activity in a bean petiole bioassay, the entire biosynthetic pathway has been elucidated (Chapter B6), receptors identified (Chapter D7), mutants characterized and crosstalk with other hormones investigated (Chapter B7).

The effects produced by each hormone were initially elucidated largely from exogenous applications. However in more and more cases we have evidence that the endogenous hormone also fulfills the originally designated roles, and new functions are being discovered. Such more recent evidence derives from correlations between hormone levels and growth of defined genotypes or mutants, particularly of the model plant Arabidopsis, or from transgenic plants. In other cases it has not yet been conclusively proved that the endogenous hormone functions in the same manner.

The nature, occurrence, transport and effects of each hormone (or hormone group) are given below. (Where there is no specific chapter on the topic in this edition but a reference in the second edition of this book (4) this is indicated with the notation '2E'.) It should, however, be emphasized that hormones do not act alone but in conjunction, or in opposition, to each other such that the final condition of growth or development represents the net effect of a hormonal balance (Chapter A2) (5).

#### Auxin

Nature

Indole-3-acetic acid (IAA) is the main auxin in most plants.

INDOLEACETIC ACID

Compounds which serve as IAA precursors may also have auxin activity (e.g., indoleacetaldehyde). Some plants contain other compounds that display weak auxin activity (e.g., phenylacetic acid). IAA may also be present as various conjugates such as indoleacetyl aspartate (Chapter B1)). 4-chloro-IAA has also been reported in several species though it is not clear to what extent the endogenous auxin activity in plants can be accounted for by 4-Cl-IAA. Several synthetic auxins are also used in commercial applications (2E: G13).

#### Sites of biosynthesis

IAA is synthesized from tryptophan or indole (Chapter B1) primarily in leaf primordia and young leaves, and in developing seeds.

#### Transport

IAA transport is cell to cell (Chapters E1 and E2), mainly in the vascular cambium and the procambial strands, but probably also in epidermal cells (Chapter E2). Transport to the root probably also involves the phloem.

#### **Effects**

- Cell enlargement auxin stimulates cell enlargement and stem growth (Chapter D1).
- Cell division auxin stimulates cell division in the cambium and, in combination with cytokinin, in tissue culture (Chapter E2 and 2E: G14).
- Vascular tissue differentiation auxin stimulates differentiation of phloem and xylem (Chapter E2).
- Root initiation auxin stimulates root initiation on stem cuttings, and also the development of branch roots and the differentiation of roots in tissue culture (2E: G14).
- Tropistic responses auxin mediates the tropistic (bending) response of shoots and roots to gravity and light (2E: G5 and G3).
- Apical dominance the auxin supply from the apical bud represses the growth of lateral buds (2E: G6).
- Leaf senescence auxin delays leaf senescence.
- Leaf and fruit abscission auxin may inhibit or promote (via ethylene) leaf and fruit abscission depending on the timing and position of the source (2E: G2, G6 and G13).
- Fruit setting and growth auxin induces these processes in some fruit (2E: G13)
- Assimilate partitioning assimilate movement is enhanced towards an auxin source possibly by an effect on phloem transport (2E: G9).
- Fruit ripening auxin delays ripening (2E: G2 & 2E:G12).
- Flowering auxin promotes flowering in Bromeliads (2E: G8).
- Growth of flower parts stimulated by auxin (2E: G2).
- Promotes femaleness in dioecious flowers (via ethylene) (2E: G2 & 2E: G8).

In several systems (e.g., root growth) auxin, particularly at high concentrations, is inhibitory. Almost invariably this has been shown to be mediated by auxin-produced ethylene (2, 7) (2E: G2). If the ethylene synthesis is prevented by various ethylene synthesis inhibitors, the ethylene removed by hypobaric conditions, or the action of ethylene opposed by silver salts (Ag+), then auxin is no longer inhibitory.

# Gibberellins (GAs)

#### Nature

The gibberellins (GAs) are a family of compounds based on the *ent*-gibberellane structure; over 125 members exist and their structures can be found on the web (Chapter B2). While the most widely available compound is  $GA_3$  or gibberellic acid, which is a fungal product, the most important GA

in plants is  $GA_1$ , which is the GA primarily responsible for stem elongation (Chapters A2, B2, and B7). Many of the other GAs are precursors of the growth-active  $GA_1$ .

GIBBERELLIN A<sub>1</sub> or GA<sub>1</sub>

#### Sites of biosynthesis.

GAs are synthesized from glyceraldehyde-3-phosphate, via isopentenyl diphosphate, in young tissues of the shoot and developing seed. Their biosynthesis starts in the chloroplast and subsequently involves membrane and cytoplasmic steps (Chapter B2).

#### **Transport**

Some GAs are probably transported in the phloem and xylem. However the transport of the main bioactive polar  $GA_1$  seems restricted (Chapters A2 and E5).

#### **Effects**

- Stem growth GA<sub>1</sub> causes hyperelongation of stems by stimulating both cell division and cell elongation (Chapters A2, B7 and D2). This produces tall, as opposed to dwarf, plants.
- Bolting in long day plants GAs cause stem elongation in response to long days (Chapter B2, 2E: G8).
- Induction of seed germination GAs can cause seed germination in some seeds that normally require cold (stratification) or light to induce germination (Chapter B2).
- Enzyme production during germination GA stimulates the production of numerous enzymes, notably  $\alpha$ -amylase, in germinating cereal grains (Chapter C3).
- Fruit setting and growth This can be induced by exogenous applications in some fruit (e.g., grapes) (2E: G13). The endogenous role is uncertain.
- Induction of maleness in dioecious flowers (2E: G8).

# Cytokinins (CKs)

#### Nature

CKs are adenine derivatives characterized by an ability to induce cell division in tissue culture (in the presence of auxin). The most common

cytokinin base in plants is zeatin. Cytokinins also occur as ribosides and ribotides (Chapter B3).

$$\begin{array}{c} CH = C \\ CH_2OH \\ CH_3 \\ CH_4 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_4 \\ CH_4 \\ CH_5 \\ CH_5$$

ZEATIN

#### Sites of biosynthesis

CK biosynthesis is through the biochemical modification of adenine (Chapter B3). It occurs in root tips and developing seeds.

#### **Transport**

CK transport is via the xylem from roots to shoots.

#### **Effects**

- Cell division exogenous applications of CKs induce cell division in tissue culture in the presence of auxin (Chapter C3; 2E: G14). This also occurs endogenously in crown gall tumors on plants (2E: E1). The presence of CKs in tissues with actively dividing cells (e.g., fruits, shoot tips) indicates that CKs may naturally perform this function in the plant.
- Morphogenesis in tissue culture (2E: G14) and crown gall (2E: E1) CKs promote shoot initiation. In moss, CKs induce bud formation (2E: G1 & G6).
- Growth of lateral buds CK applications, or the increase in CK levels in transgenic plants with genes for enhanced CK synthesis, can cause the release of lateral buds from apical dominance (2E: E2 & G6).
- Leaf expansion (6), resulting solely from cell enlargement. This is probably the mechanism by which the total leaf area is adjusted to compensate for the extent of root growth, as the amount of CKs reaching the shoot will reflect the extent of the root system. However this has not been observed in transgenic plants with genes for increased CK biosynthesis, possibly because of a common the lack of control in these systems.
- CKs delay leaf senescence (Chapter E6).
- CKs may enhance stomatal opening in some species (Chapter E3).
- Chloroplast development the application of CK leads to an accumulation of chlorophyll and promotes the conversion of etioplasts into chloroplasts (8).

#### **Ethylene**

#### Nature

The gas ethylene ( $C_2H_4$ ) is synthesized from methionine (Chapter B4) in many tissues in response to stress, and is the fruit ripening hormone. It does not seem to be essential for normal mature vegetative growth, as ethylene-deficient transgenic plants grow normally. However they cannot, as seedlings, penetrate the soil because they lack the stem thickening and apical hook responses to ethylene, and they are susceptible to diseases because they lack the ethylene-induced disease resistance responses. It is the only hydrocarbon with a pronounced effect on plants.

#### Sites of synthesis

Ethylene is synthesized by most tissues in response to stress. In particular, it is synthesized in tissues undergoing senescence or ripening (Chapters B4 and E5).

#### **Transport**

Being a gas, ethylene moves by diffusion from its site of synthesis. A crucial intermediate in its production, 1-aminocyclopropane-1-carboxylic acid (ACC) can, however, be transported and may account for ethylene effects at a distance from the causal stimulus (2E: G2).

# **Effects**

The effects of ethylene are fully described in 2E: G2. They include:

- The so called *triple response*, when, prior to soil emergence, dark grown seedlings display a decrease in tem elongation, a thickening of the stem and a transition to lateral growth as might occur during the encounter of a stone in the soil.
- Maintenance of the apical hook in seedlings.
- Stimulation of numerous defense responses in response to injury or disease.
- Release from dormancy.
- Shoot and root growth and differentiation.
- Adventitious root formation.
- Leaf and fruit abscission.
- Flower induction in some plants (2E: G8).
- Induction of femaleness in dioecious flowers (2E: 8).
- Flower opening.
- Flower and leaf senescence.
- Fruit ripening (Chapters B4 and E5).

# Abscisic acid (ABA)

#### Nature

Abscisic acid is a single compound with the following formula:

ABSCISIC ACID

Its name is rather unfortunate. The first name given was "abscisin II" because it was thought to control the abscission of cotton bolls. At almost the same time another group named it "dormin" for a purported role in bud dormancy. By a compromise the name abscisic acid was coined (1). It now appears to have little role in either abscission (which is regulated by ethylene; 2E: G2) or bud dormancy, but we are stuck with this name. As a result of the original association with abscission and dormancy, ABA has become thought of as an inhibitor. While exogenous applications can inhibit growth in the plant, ABA appears to act as much as a promoter, such as in the promotion of storage protein synthesis in seeds (Chapter E4), as an inhibitor, and a more open attitude towards its overall role in plant development is warranted. One of the main functions is the regulation of stomatal closure (Chapters D6 and E3)

# Sites of synthesis

ABA is synthesized from glyceraldehyde-3-phosphate via isopentenyl diphosphate and carotenoids (Chapter B5) in roots and mature leaves, particularly in response to water stress (Chapters B5 and E3). Seeds are also rich in ABA which may be imported from the leaves or synthesized in situ (Chapter E4).

#### **Transport**

ABA is exported from roots in the xylem and from leaves in the phloem. There is some evidence that ABA may circulate to the roots in the phloem and then return to the shoots in the xylem (Chapters A2 and E4).

# **Effects**

- Stomatal closure water shortage brings about an increase in ABA which leads to stomatal closure (Chapters D6 and E3).
- ABA inhibits shoot growth (but has less effect on, or may promote, root growth). This may represent a response to water stress (Chapter E3; 2E: 2).
- ABA induces storage protein synthesis in seeds (Chapter E4).
- ABA counteracts the effect of gibberellin on  $\alpha$ -amylase synthesis in germinating cereal grains (Chapter C2).
- ABA affects the induction and maintenance of some aspects of dormancy in seeds (Chapters B5 and E4). It does not, however, appear

- to be the controlling factor in 'true dormancy' or 'rest,' which is dormancy that needs to be broken by low temperature or light.
- Increase in ABA in response to wounding induces gene transcription, notably for proteinase inhibitors, so it may be involved in defense against insect attack (2E: E5).

#### **Polyamines**

$$H_2N$$
— $(CH_2)_3$ — $NH$ — $(CH_2)_4$ — $NH_2$   
SPERMIDINE

Polyamines are a group of aliphatic amines. The main compounds are putrescine, spermidine and spermine. They are derived from the decarboxylation of the amino acids arginine or ornithine. The conversion of the diamine putrescine to the triamine spermidine and the quaternaryamine spermine involves the decarboxylation of S-adenosylmethionine, which also is on the pathway for the biosynthesis of ethylene. As a result there are some complex interactions between the levels and effects of ethylene and the polyamines.

The classification of polyamines as hormones is justified on the following grounds:

- They are widespread in all cells and can exert regulatory control over growth and development at micromolar concentrations.
- In plants where the content of polyamines is genetically altered, development is affected. (E.g., in tissue cultures of carrot or *Vigna*, when the polyamine level is low only callus growth occurs; when polyamines are high, embryoid formation occurs. In tobacco plants that are overproducers of spermidine, anthers are produced in place of ovaries.)

Such developmental control is more characteristic of hormonal compounds than nutrients such as amino acids or vitamins.

Polyamines have a wide range of effects on plants and appear to be essential for plant growth, particularly cell division and normal morphologies. At present it is not possible to make an easy, distinct list of their effects as for the other hormones. Their biosynthesis and a variety of cellular and organismal effects is discussed in 2E Chapter C1. It appears that polyamines are present in all cells rather than having a specific site of synthesis.

#### **Brassinosteroids**

Brassinosteroids (Chapters B6 and D7) are a range of over 60 steroidal compounds, typified by the compound brassinolide that was first isolated from *Brassica* pollen. At first they were regarded as somewhat of an oddity but they are probably universal in plants. They produce effects on growth and development at very low concentrations and play a role in the endogenous regulation of these processes.

## **Effects**

- Cell Division, possibly by increasing transcription of the gene encoding cyclinD3 which regulates a step in the cell cycle (Chapter D7).
- Cell elongation, where BRs promote the transcription of genes encoding xyloglucanases and expansins and promote wall loosening (Chapter D7). This leads to stem elongation.
- Vascular differentiation (Chapter D7).
- BRs are needed for fertility: BR mutants have reduced fertility and delayed senescence probably as a consequence of the delayed fertility (Chapter D7).
- Inhibition of root growth and development
- Promotion of ethylene biosynthesis and epinasty.

#### Jasmonates

Jasmonates (Chapter F1) are represented by jasmonic acid (JA) and its methyl ester.

#### **JASMONIC ACID**

They are named after the jasmine plant in which the methyl ester is an important scent component. As such they have been known for some time in the perfume industry. There is also a related hydroxylated compound that has been named tuberonic acid which, with its methyl ester and glycosides, induces potato tuberization (Chapter E5). Jasmonic acid is synthesized from linolenic acid (Chapter F1), while jasmonic acid is most likely the precursor of tuberonic acid.

# **Effects**

• Jasminates play an important role in plant defense, where they induce

the synthesis of proteinase inhibitors which deter insect feeding, and, in this regard, act as intermediates in the response pathway induced by the peptide systemin.

- Jamonates inhibit many plant processes such as growth and seed germination.
- They promote senescence, abscission, tuber formation, fruit ripening, pigment formation and tendril coiling.
- JA is essential for male reproductive development of Arabidopsis. The role in other species remains to be determined.

## Salicylic Acid (SA)



SALICYLIC ACID

Salicylates have been known for a long time to be present in willow bark, but have only recently been recognized as potential regulatory compounds. Salicylic acid is biosynthesized from the amino acid phenylalanine.

#### **Effects**

- Salicylic acid (Chapter F2) plays a main role in the resistance to pathogens by inducing the production of 'pathogenesis-related proteins'. It is involved in the systemic acquired resistance response (SAR) in which a pathogenic attack on older leaves causes the development of resistance in younger leaves, though whether SA is the transmitted signal is debatable.
- SA is the calorigenic substance that causes thermogenesis in *Arum* flowers.
- It has also been reported to enhance flower longevity, inhibit ethylene biosynthesis and seed germination, block the wound response, and reverse the effects of ABA

# **Signal Peptides**

The discovery that small peptides could have regulatory properties in plants started with the discovery of systemin, an 18 amino acid peptide that travels in the phloem from leaves under herbivore insect attack to increase the content of jasmonic acid and proteinase inhibitors in distant leaves, so protecting them from attack (Chapters F1 and F3). Since then, over a dozen peptide hormones that regulate various processes involved in defense, cell

division, growth and development and reproduction have been isolated from plants, or identified by genetic approaches (Chapter F3). Among these effects caused by specific peptides are:

- The activation of defense responses.
- The promotion of cell proliferation of suspension cultured plant cells.
- The determination of cell fate during development of the shoot apical meristem
- The modulation of root growth and leaf patterning in the presence of auxin and cytokinin
- Peptide signals for self-incompatability.
- Nodule formation in response to bacterial signals involved in nodulation in legumes.

## Are the More-Recently-Discovered Compounds Plant Hormones?

Two decades ago there was a heated discussion as to whether a compound had to be transported to be a plant hormone, and could ethylene therefore be a plant hormone. To this Carl Price responded: "Whether or not we regard ethylene as a plant hormone is unimportant; bananas do..." Hormones are a human classification and organisms care naught for human classifications. Natural chemical compounds affect growth and development in various ways, or they do not do so. Clearly brassinosteroids fit the definition of a plant hormone, and likely polyamines, jasmonates salicylic acid and signal peptides also can be so classified. Whether other compounds should be regarded as plant hormones in the future will depend on whether, in the long run, these compounds are shown to be endogenous regulators of growth and development in plants in general.

# A Selection of Books on Plant Hormones Detailing their Discovery and Effects

Abeles FB, Morgan PW, Saltveit ME (1992) Ethylene in Plant Biology. Academic Press, San Diego

Addicott FT (ed) (1983) Abscisic acid. Praeger, New York

Arteca RN (1995) Plant Growth Substances, Principles and Applications. Chapman and Hall, New York

Audus LJ (1959) Plant Growth Substances (2E) L. Hill, London; Interscience Publishers New York. (Editors note: the 2<sup>nd</sup> edition of Audus contains a lot of information on auxins that was cut out of the later, broader, 3<sup>rd</sup> edition and it is therefore still a valuable reference.)

Audus LJ (1972) Plant Growth Substances (3E). Barnes & Noble, New York

Crozier A (ed) (1983) The Biochemistry and Physiology of Gibberellins. Praeger, New York Davies PJ (ed) (1995) Plant Hormones: Physiology, Biochemistry and Molecular Biology. Kluwer Academic, Dordrecht, Boston

Davies WJ, Jones HG (1991) Abscisic Acid: Physiology and Biochemistry. Bios Scientific Publishers, Oxford, UK

Hayat S, Ahmad A (eds) (2003) Brassinosteroids: Bioactivity and Crop Productivity. Kluwer Academic, Dordrecht, Boston

.

<sup>&</sup>lt;sup>3</sup> Carl A. Price, in Molecular Approaches to Plant Physiology

Jacobs WP (1979) Plant Hormones and Plant Development. Cambridge University Press

Khripach VA, Zhabinskii VN, de Groot AE (1999) Brassinosteroids: A New Class of Plant Hormones, Academic Press, San Diego

Krishnamoorthy HN (1975) Gibberellins and Plant Growth. Wiley, New York

Mattoo A, Suttle J (1991) The Plant Hormone Ethylene. CRC Press Boca Raton FL

Mok DWS, Mok MC (1994) Cytokinins: Chemistry, Activity and Function. CRC Press Boca Raton FL

Sakurai A, Yokota T, Clouse SD (eds) (1999) Brassinosteroids: Steroidal Plant Hormones Springer, Tokyo, New York

Slocum RD, Flores HE (eds) (1991) Biochemistry and Physiology of Polyamines in Plants. Boca Raton CRC Press

Thimann KV (1977) Hormone Action in the Whole Life of Plants. University of Massachusetts Press, Amherst

Takahashi N, Phinney BO, MacMillan J (eds) (1991) Gibberellins. Springer-Verlag, New York

Yopp JH, Aung, LH, Steffens GL (1986) Bioassays and Other Special Techniques for Plant Hormones and Plant Growth Regulators. Plant Growth Regulator Society of America Lake Alfred FL, USA

#### References

- Addicott FT, Carns HR, Cornforth JW, Lyon JL, Milborrow BV, Ohkuma K, Ryback G, Thiessen WE, Wareing PF (1968) Abscisic acid: a proposal for the redesignation of abscisin II (dormin). In F Wightman, G Setterfield, eds, Biochemistry and Physiology of Plant Growth Substances, Runge Press, Ottawa, pp 1527-1529
- 2. Burg SP, Burg EA (1966) The interaction between auxin and ethylene and its role in plant growth. Proc Natl Acad Sci USA 55: 262-269
- 3. Darwin C (1880) The power of movement in plants. John Murray, London,
- 4. Davies PJ (1995) Plant Hormones: Physiology, Biochemistry and Molecular Biology. Kluwer Academic Publishers. Dordrecht. The Netherlands: Norwell. MA. USA.
- 5. Leopold AC (1980) Hormonal regulating systems in plants. In SP Sen, ed, Recent Developments in Plant Sciences, Today and Tomorrow Publishers, New Delhi, pp 33-41
- 6. Letham DS (1971) Regulators of cell division in plant tissues. XII. A cytokinin bioassay using excised radish cotyledons. Physiol Plant 25: 391-396
- 7. Mulkey TJ, Kuzmanoff KM, Evans ML (1982) Promotion of growth and hydrogen ion efflux by auxin in roots of maize pretreated with ethylene biosynthesis inhibitors. Plant Physiol 70: 186-188
- 8. Parthier B (2004) Phytohormones and chloroplast development. Biochem Physiol Pflanz 174: 173-214
- 9. Phinney BO (1983) The history of gibberellins. In A Crozier, ed, The Biochemistry and Physiology of Gibberellins, Vol 1. Praeger, New York, pp 15-52
- 10. Went FW, Thimann KV (1937) Phytohormones. Macmillan, New York,
- Wildman SG (1997) The auxin-A, B enigma: Scientific fraud or scientific ineptitude? Plant Growth Regul 22: 37-68

actually been distributed and sold. If inspection of products released for shipment could not lead directly to enforcement action, but must await some further point at which it had been "distributed and sold," the Agency's enforcement efforts would be thwarted.

Consequently, in the final rule, the Agency has included the term "released for shipment" in the definition of

"distribute and sell."

The Agency also considered defining the term "channels of trade," which has been used in past Agency documents (without definition) as an informal synonym for the litany of terms in FIFRA sec. 12 comprising "distribute and sell." EPA considers the two terms synonymous: a product that is being distributed and sold by any person is in channels of trade, and vice versa. It is therefore unnecessary to define "channels of trade" separately. Moreover, the Agency does not expect to use the term in future regulatory documents, but will rather specify the categories of persons who are prohibited from distributing or selling a product. Thus, the registrant may be prohibited from distributing or selling after a certain date, while other persons (e.g., retailers) may be prohibited from distributing or selling after a second

#### IV. Products Required To Be Registered

The Agency proposed to clarify its o interpretation of what constitutes a pesticide, for purposes of compliance with the registration requirement of FIFRA sec. 3. Section 152.15 proposed to add new language stating that a substance may be intended for a pesticidal purpose (and therefore required to be registered) if any of a number of tests are met. The first of these is whether advertising or product labeling claims, implicitly or explicitly, that the product is a pesticide. This is the principal test contained in current regulations. No comments were received on this test, and it has been adopted as proposed.

EPA also proposed to treat as a pesticide any substance which has no significant commercially valuable use other than a pesticidal one. One commenter objected that the term "significant commercially valuable use" is judgmental. EPA acknowledges that a certain degree of judgment must be exercised in deciding whether a substance meets this definition. On the other hand, the Agency believes that a large percentage, if not the majority, of pesticide active ingredients are clearly identifiable either as pesticides or as multi-purpose substances, and that the Agency will rarely be compelled to use

this criterion alone to judge whether a substance is a pesticide. The Agency has in the past focused its enforcement efforts on individual product claims, and EPA intends to continue this focus.

The Agency further proposed, as a third criterion, that if a person knows, or should reasonably know, that he is selling a product for a pesticidal purpose (even though the product itself bears no pesticidal claims), the product should be a pesticide subject to the registration requirement. This criterion would apply primarily to products which are currently not registered as pesticides (for example, multi-purpose substances having pesticide uses, but for which a particular product bears no pesticidal claims.)

Nine persons commented upon this provision. Several expressed concern that the language was imputing knowledge of pesticidal use and responsibility to manufacturers who have no control over their distributors and customers. This burden, they state, is unreasonable. Other commenters, while not objecting to the criterion per se, requested that the Agency clarify its intent, and sought reassurance that the criterion would be used for enforcement against the person making the claim and not against the producer. Some suggested that simply deleting the word "reasonably" from the criterion would resolve the problem satisfactorily. In general, commenters believed that definition was too broad and inclusive.

In response, the Agency has clarified the definition by replacing the "reasonable" knowledge terminology with language concerning "actual or constructive" knowledge of pesticidal use. Actual or constructive knowledge will be gauged as objectively as possible. The Agency issued in the Federal Register of March 25, 1987 (52 FR 9504) a proposal concerning establishment registration, which uses, the same terminology to describe when a pesticide producer must register his producing establishment. In that document, the Agency described the criteria that it would consider in determining actual or constructive knowledge. These included promotional claims and advertising, common knowledge of the general business of the person to whom the substance is sold, and the commercial distance from a producer to a formulator. The same principles will guide the Agency in applying the "actual or constructive knowledge" test of pesticide for purposes of registration.

The Agency believes the fears of the

The Agency believes the fears of the commenters concerning "upstream penalties" are unfounded. The Agency does not intend to impose penalties

upon the producer of a non-pesticide product, if, without his knowledge, a pesticidal claim is made for the product by someone else. EPA agrees that it would be unreasonable to require registration of a product whose primary uses are non-pesticidal merely because a retailer sold the product as a pesticide. On the other hand, EPA believes that a producer who sells a product with full knowledge of its intended pesticidal use should be held responsible for its registration. This situation might apply, for example, when a producer sells what would ordinarily be considered a basic chemical to a user whose only purpose in acquiring such a chemical would be to use it as a pesticide. If the seller of the product is aware of the nature of his customer's business, EPA may consider him to be selling a product for a pesticidal purpose. EPA acknowledges that application of this criterion for enforcement purposes will require subjective judgment.

The second and third criteria both are intended to address longstanding enforcement problems in which neither labeling nor advertising clearly states or implies that the product is a pesticide, but the product is sold under circumstances in which it is clear that the product is intended for a pesticidal purpose. For example, if the ingredients of a well-known wood preservative mixture are offered for sale (without pesticidal claims) in a trade magazine aimed primarily at wood processors and there is no other apparent reason for wood processors to be interested in the ingredients, it would not be unreasonable to regard the products as pesticides.

#### V. Exemptions

#### A. Exemptions under FIFRA Sec. 25(b)

Sections 152.20 and 152.25 describe exemptions based on FIFRA sec. 25(b) for, respectively, products adequately regulated by another Federal agency and products of a character not requiring FIFRA regulation.

One commenter suggested that the exemption for pheromones in § 152.25(a) be expanded to include pheromones other than those produced by an arthropod. Paragraph (a)(1) of that section defines a pheromone as a compound produced by arthropods. The Agency declines to adopt the commenter's suggestion. The Agency is not aware that pheromones produced by other animals are registered with the Agency. EPA was able to exempt arthropod pheromones based on information it possessed in its files on such products. Although the Agency

#### A. Definitions

Current § 162.3 would be revised to add new definitions, to delete unnecessary or obsolete ones, and to clarify existing definitions. In general, definitions pertaining to labeling requirements would be transferred to proposed Part 156. Definitions that are used throughout Part 152 would be included in the principal definitions section of Subpart A. Definitions that apply to only one subpart would be located at the beginning of that subpart. Changes of note include the following:

1. The term "distribute or sell" and its grammatical variations would be defined. These terms are used in the Act to define the activities concerning pesticides to which FIFRA applies and at which point the Agency is authorized to regulate. This proposal defines the term to encompass the term "released for shipment," which is used in defining EPA's inspection authority under FIFRA sec. 9. The term "released for shipment" has not been used in FIFRA regulations before, but has been defined in policy statements in the same manner as proposed here.

2. Under FIFRA-section 3(b)(1) products may be shipped between establishments "operated by the same producer" without registration. The current definition encompasses both establishments owned by a single producer, and also establishments operated under contract to a producer, but which may be owned by another person. In this proposal, the Agency would define the phrase "operated by the same producer" to limit it to establishments owned or leased by a single company. Limiting the definition in this manner EPA believes would reflect the intent of Congress in FIFRA section 3(b)(1) and the clear sense of the phrase.

The provision for shipment between one producer and another under contract for processing, packaging and labeling (permitted without registration under the current definition of "operated by the same producer") would be continued by specific exemption in § 152.30. The contractual exemption is discussed later in this preamble.

3. The term "domestic application" would be replaced with the terms "residential use" and "institutional use," to allow better delineation of the applicability of certain requirements, (such as child-resistant packaging, which is required for products labeled for residential use but not for products labeled for institutional use). The definition of residential use would include those areas contained in the "domestic" use definition that clearly

relate to household use sites, and would include also pre-school and day care facilities where small children spend time. Institutional use would include larger facilities such as hospitals, office buildings, commercial establishments. and schools at the elementary or above level, which the Agency believes have different pesticide use and exposure patterns. The Agency requests comments on whether these definitions are adequate for the purpose of this regulation, or whether they should be modified, and in what ways, to be more useful. In particular, EPA would like comment on whether day care and preschool facilities should be encompassed by the residential use definition.

#### B. When Registration Is Required

Under FIFRA sec. 3, a pesticide must be registered before it can be distributed or sold. FIFRA section 2(u) defines a pesticide in terms of its intended use against a pest, or its use for pesticidal purposes. Whether a substance is a pesticide that must be registered depends on the interpretation of pest, pesticidal purpose, and the intent of use of a product as a pesticide.

The term "pesticide" has different meanings in different portions of the Act. In some places it is used as a general term to describe substances which are subject to the Act. In other places, it is used to mean a particular pesticide product that is distributed or sold, and which, according to FIFRA section 3, must be registered. This proposal will use the term "pesticide" in its general sense; the term "pesticide product" will be used to describe a particular pesticide in the form in which it is (or will be) registered and marketed. including the product's composition. packaging and labeling.

The proposal further elaborates on the meaning of concepts ("pest," "pesticidal purpose," and "intent" that the Agency uses in deciding whether a substance is a pesticide product which must be registered. Sections 152.8, 152.10, and 152.15 of the proposal would set out exclusions from registration based on these factors.

First, a pesticide product may be subject to registration only if it is intended for use against a pest (or for use as a plant regulator, desiccant or defoliant). The Administrator must define those organisms deemed to be pests for the purposes of the Act. Section 152.5 would define as pests vertebrates, invertebrates, insects, fungi, weeds, and microorganisms which are deleterious to man or the environment.

Second, a pesticide product will be subject to registration only if it is

intended to produce a "pesticidal effect." A substance may function against a pest without having a pesticidal effect. An example would be a product used for survey and detection purposes rather than pesticidal purposes. Section 152.10 lists products which do not have a pesticidal effect, and therefore are not required to be registered.

Finally, it is not enough that a substance have a "pesticidal effect" on a "pest;" the substance must also be "intended" to have that effect. Thus, a substance is a pesticidal product that may be subject to registration if, regardless of whether it actually has a pesticidal effect, it is intended to be used for a pesticidal purpose. The determination of intent is a separate test for the requirement for registration, and is central to the decision of whether a product is required to be registered.

Section 152.15 would describe the circumstances under which the Agency will presume that a substance is being distributed and sold with the intent that it be used as a pesticide. Clearly, either express or implied claims or representations by the seller, such as labeling or advertising, would be evidence of intent. However, the Agency believes that, in the absence of claims, a product may be considered to be a pesticide if the seller or distributor is aware of the intended uses of the product as a pesticide. This may be the case either because there are no other significant uses of the product, or because other circumstances of the sale and distribution are such that he should reasonably know the ultimate use of the product as a pesticide.

# C. Exemptions Under FIFRA

FIFRA section 25 authorizes the Administrator to exempt from any or all provisions of FIFRA a pesticide for which he can make a determination that the pesticide either is adequately regulated by another Federal agency or is of such a character that regulation under FIFRA is not necessary.

The Agency is given the latitude to determine the scope of an exemption under FIFRA section 25. Although a producer may be relieved of the provisions of all or any sections of FIFRA by an exemption, as a practical matter only two levels of exemption are viewed as cost-efficient for both Agency and producer: exemption from all provisions of FIFRA or exemption from the registration requirements of FIFRA section 3. This proposal contains two sections devoted to exemptions. These sections would be used to list pesticides exempted partly or wholly from FIFRA

# University of Florida IFAS Extension

Solutions for Your Life

**EDIS** 

Home FAQs & Help Local Offices IFAS Bookstore Advanced Search



Download PDF 📆

Publication #HS1208

Topics: Hanlon, Edward A | Fertilization and Nutrition | Liu, Guodong | Li, Yuncong | Horticultural Sciences

# Understanding and Applying Chelated Fertilizers Effectively Based on Soil pH<sup>1</sup>



Guodong Liu, Edward Hanlon, and Yuncong Li<sup>2</sup>

Plant nutrients are one of the environmental factors essential for crop growth and development. Nutrient management is crucial for optimal productivity in commercial crop production. Those nutrients in concentrations of = 100 parts per million (ppm) in plant tissues are described as micronutrients and include iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), chlorine (Cl), molybdenum (Mo), and nickel (Ni). Micronutrients such as Fe, Mn, Zn, and Cu are easily oxidized or precipitated in soil, and their utilization is, therefore, not very efficient. Chelated fertilizers have been developed to increase micronutrient utilization efficiency. This publication provides an overview of chelated fertilizers and considerations for their use to county Extension faculty, certified crop advisers, crop consultants, growers, and students who are interested in commercial crop production.

#### What is chelated fertilizer?

The word *chelate* is derived from the Greek word *chelé*, which refers to a lobster's claw. Hence, chelate refers to the pincer-like manner in which a metal nutrient ion is encircled by the larger organic molecule (the claw), usually called a ligand or chelator. Table 1 lists common natural or chemical synthetic ligands (Havlin et al. 2005; Sekhon 2003). Each of the listed ligands, when combined with a micronutrient, can form a chelated fertilizer. Chelated micronutrients are protected from oxidation, precipitation, and immobilization in certain conditions because the organic molecule (the ligand) can combine and form a ring encircling the micronutrient. The pincer-like manner in which the micronutrient is bonded to the ligand changes the micronutrient's surface property and favors the uptake efficiency of foliarly applied micronutrients.

#### Why is chelated fertilizer needed?

Because soil is heterogeneous and complex, traditional micronutrients are readily oxidized or precipitated. Chelation keeps a micronutrient from undesirable reactions in solution and soil. The chelated fertilizer improves the bioavailability of micronutrients such as Fe, Cu, Mn, and Zn, and in turn contributes to the productivity and profitability of commercial crop production. Chelated fertilizers have a greater potential to increase commercial yield than regular micronutrients if the crop is grown in low-micronutrient stress or soils with a pH greater than 6.5. To grow a good crop, crop nutrient requirements (CNRs), including micronutrients, have to be satisfied first from the soil. If the soil cannot meet the CNR, chelated sources need to be used. This approach benefits the plant without increasing the risk of eutrophication.

Several factors reduce the bioavailability of Fe, including high soil pH, high bicarbonate content, plant species (grass species are usually more efficient than other species because they can excrete effective ligands), and abiotic stresses. Plants typically utilize iron as ferrous iron (Fe<sup>2+</sup>). Ferrous iron can be readily oxidized to the plant-unavailable ferric form (Fe<sup>3+</sup>) when soil pH is greater than 5.3 (Morgan and Lahav 2007). Iron deficiency often occurs if soil pH is greater than 7.4. Chelated iron can prevent this conversion from Fe<sup>2+</sup> to Fe<sup>3+</sup>.

Applying nutrients such as Fe, Mn, Zn, and Cu directly to the soil is inefficient because in soil solution they are present as positively charged metal ions and will readily react with oxygen and/or negatively charged hydroxide ions (OH<sup>-</sup>). If they react with oxygen or hydroxide ions, they

form new compounds that are not bioavailable to plants. Both oxygen and hydroxide ions are abundant in soil and soilless growth media. The ligand can protect the micronutrient from oxidization or precipitation. Figure 1 shows examples of the typical iron deficiency symptoms of lychee grown in Homestead, Florida, in which the lychee trees have yellow leaves and small, abnormal fruits. Applying chelated fertilizers is an easy and practical correction method to avoid this nutrient disorder. For example, the oxidized form of iron is ferric (Fe<sup>3+</sup>), which is not bioavailable to plants and usually forms brown ferric hydroxide precipitation (Fe(OH)<sub>3</sub>). Ferrous sulfate is often used as the iron source. Its solution should be green. If the solution turns brown, the bioavailable form of iron has been oxidized and Fe is therefore unavailable to plants.

In the soil, plant roots can release exudates that contain natural chelates. The nonprotein amino acid, mugineic acid, is one such natural chelate called phytosiderophore (phyto: plant; siderophore: iron carrier) produced by graminaceous (grassy) plants grown in low-iron stress conditions. The exuded chelate works as a vehicle, helping plants absorb nutrients in the root-solution-soil system (Lindsay 1974). A plant-excreted chelate forms a metal complex (i.e., a coordination compound) with a micronutrient ion in soil solution and approaches a root hair. In turn, the chelated micronutrient near the root hair releases the nutrient to the root hair. The chelate is then free and becomes ready to complex with another micronutrient ion in the adjacent soil solution, restarting the cycle. The process works like this:

A chelate is exuded from a root to the soil solution.

The chelate complexes a micronutrient (e.g., iron) from the soil solution.

The chelated micronutrient is carried to a root hair, where it is released.

The chelate goes back to the soil solution and starts another cycle.



Figure 1. Typical iron deficiency symptoms of lychee (*Litchi chinensis*, the soapberry family).

Credit: Yuncong Li

[Click thumbnail to enlarge.]

Chemical reactions between micronutrient chelates and soil can be avoided by using a foliar application. Chelated nutrients also facilitate nutrient uptake efficiency for foliar application because crop leaves are naturally coated with wax that repels water and charged substances, such as ferrous ions. The organic ligand around the chelated micronutrient can penetrate the wax layer, thus increasing iron uptake (Figure 2). Compared to traditional iron fertilization, chelated iron fertilization is significantly more effective and efficient (Figure 3).

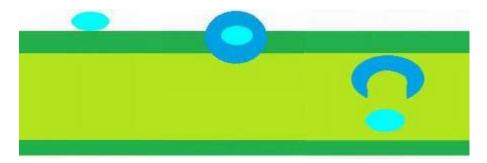


Figure 2. Schematic diagram of chelated fertilizers facilitating nutrient uptake for foliar application. Without chelation (aqua), micronutrients stay on the leaf surface. With chelation (aqua surrounded by blue), micronutrients first move into the mesophyll and then release micronutrients. Color key: aqua = a micronutrient ion; blue = organic ligand; dark green = wax layer on leaves; light green = mesophyll.

Credit: Fullerton 2004

[Click thumbnail to enlarge.]



Figure 3. Comparison of foliar applications of chelated Fe, regular iron fertilizers, and no iron fertilization on correcting iron deficiency of lychee (*Litchi chinensis*, the soapberry family).

Credit: Yuncong Li
[Click thumbnail to enlarge.]

Therefore, chelated fertilization can improve micronutrient use efficiency and make micronutrient fertilization more cost effective. The images in Figure 3 show the difference in three treatments with lychee: chelated Fe(II) is greener than FeSO<sub>4</sub> plus sulfuric acid, and FeSO<sub>4</sub> plus sulfuric acid is greener than no iron fertilization (Schaffer et al. 2011).

### Which crops often need chelated fertilizers?

Vegetable and fruit crop susceptibility to micronutrients differs significantly (Table 2). For those in the highly or moderately susceptible categories, chelated fertilizers are often needed. For those with low susceptibility, generally speaking, no chelated fertilizers are needed unless the soil is low in micronutrient bioavailability, as demonstrated by a soil test. Soil pH is a major factor influencing micronutrient bioavailability; therefore, if soil pH is greater than 6.5, then the soil may have limited micronutrient bioavailability (Poh et al. 2009), and chelated fertilizers may be needed.

### Which chelated fertilizer should be used?

Each of the ligands (Table 1) can form a chelated fertilizer with one or more micronutrients. The effectiveness and efficiency of a particular chelated fertilizer depends on the pH of the plant growth medium.

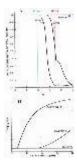


Figure 4. Effects of pH and chelate species, including EDTA, OTPA, and EDDHA, on chelated iron stability (A) and on crop yield (B) Credit: (A) Havlin et al. 2005; Norvell 1972, (B) Havlin et al. 2005; Lindsay 1974

[Click thumbnail to enlarge.]

The ligands EDTA, DTPA, and EDDHA are often used in chelated fertilizers (Table 4). Their effectiveness differs significantly. Generally speaking, EDDHA chelated Fe is most stable at soil pH greater than 7 (Figure 4, A and B). Chelated fertilizer stability is desired because it means the chelated micronutrient will remain in a bioavailable form for a much longer time period, thus increasing micronutrient use efficiency in vegetable and fruit production. The stability of three typical chelated Fe fertilizers varies at different pH conditions (Figure 4, A). The Y-axis represents the ratio of chelated Fe to total chelate and ranges from 0 to 1.0. A value of 1.0 means the chelate is stable. The X-axis represents soil pH. At 6.0, the ratios for all of the three chelated Fe fertilizers are 1.0 (stable), but at pH 7.5, only the ratio of EDDTA chelated Fe is 1.0. That of DTPA chelated Fe is only 0.5, and that of EDTA chelated Fe is only 0.025. So, in practice, EDDTA chelated Fe fertilizer is

most effective when pH is greater than 7 but most costly. Accordingly, crop yields of these three chelated fertilizers are in this order: FeEDDHA > FeEDTA (Figure 4, B). See *Micronutrient Deficiencies in Citrus: Iron, Zinc, and Manganese* (http://edis.ifas.ufl.edu/ss423) for effective pH ranges of iron chelates. Table 3 shows the relationship between soil pH and chelated fertilizer requirement.

Correction of Fe deficiency depends on individual crop response and many other factors. For instance, for vegetables, the rate is usually 0.4–1 lb. chelated Fe in 100 gal. of water per acre. Deciduous fruits need 0.1–0.2 lb. chelated Fe in 25 gal. of water per acre (Table 5). Foliar application is more effective than soil application. For foliar application, either inorganic or chelated Fe is effective, but for fertigation, chelated Fe should be used. In high pH soil, crops are also vulnerable to Cu deficiency stresses. Chelated Cu is significantly more effective than inorganic Cu. A commonly used copper chelate is Na<sub>2</sub>CuEDTA, which contains 13% Cu. Natural organic materials have approximately 0.5% Cu (Table 5).

In addition to soil pH, Mn is also influenced by aeration, moisture, and organic matter content. Chelated Mn can improve Mn bioavailability. Mn deficiency occurs more often in high pH and dry soil. Similar to other micronutrients, foliar spray is much more effective than soil application. For commercial vegetable production, 0.2–0.5 lb. MnEDTA in 200 gal. of water per acre can effectively correct Mn deficiency (Table 5). Zinc is another micronutrient whose bioavailability is closely associated with soil pH. Crops may be susceptible to Zn deficiency in soil with pH > 7.3. Spraying 0.10–0.14 lb. chelated Zn in 100 gal. of water per acre is effective (Poh et al. 2009). Animal waste and municipal waste also contain Cu, Mn, and Zn micronutrients (Table 5). For more information about micronutrient deficiency in crops, see *Plant Tissue Analysis and Interpretation for Vegetable Crops in Florida* (http://edis.ifas.ufl.edu/ep081), *Micronutrient Deficiencies in Citrus: Iron, Zinc, and Manganese* (http://edis.ifas.ufl.edu/ss555).

#### **Practical Take-Home Message**

- High pH soil (pH > 6.5) often has low bioavailability in micronutrients such as Fe, Mn, Zn, and Cu, and micronutrient fertilizers are needed for commercial crop production.
- Crop susceptibility to the above micronutrients depends on the species and cultivar. Commercial crops can be categorized into three susceptibility groups: high, medium, and low. The first two groups often need chelated fertilizers.
- Inorganic water-soluble micronutrient application to the soil is often ineffective for correcting micronutrient disorders.
- Chelated fertilizers are less reactive to soil conditions and can significantly enhance nutrient uptake and utilization efficiencies.
- Chelate fertilization rates range from 0.2 to 1 lb. micronutrient per acre for vegetable production and 0.1–0.5 lb. micronutrient per acre for fruit production.
- Foliar application of chelated fertilizers is often more effective than soil application.

#### References

Alloway, B. J. 2008. *Micronutrient Deficiencies in Global Crop Production*. Herdelberg, Germany: Springer Science + Business Media, B. V. Berlin.

Fullerton, T. 2004. "Chelated Micronutrients." Agro Services International Inc. http://www.agroservicesinternational.com/Articles/Chelates.pdf.

Havlin, J. L., J. D. Beaton, S. L. Tisdale, and W. L. Nelson. 2005. *Soil Fertility and Fertilizers: An Introduction to Nutrient Management* (7<sup>th</sup> ed.). Upper Saddle River, NJ: Pearson Education.

Lindsay, W. L. 1974. "Role of Chelation in Micronutrient Availability." In: *The Plant Root and Its Environment*, edited by E. E. Carson, 507-524. Charlottesville: University Press of Virginia.

Morgan, B., and O. Lahav. 2007. "The Effect of pH on the Kinetics of Spontaneous Fe (II) Oxidation by O<sub>2</sub> in Aqueous Solution – Basic Principles and a Simple Heuristic Description." *Chemosphere* 68(11): 2080–2084.

Norvell, W. A. 1972. "Equilibria of Metal Chelates in Soil Solution." In *Micronutrients in Agriculture*, edited by J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay, 115–136. Madison, WI: Soil Science Association of America.

Poh, B. L., A. Gevens, E. Simonne, and C. Snodgrass. 2009. *Estimating Copper, Manganese and Zinc Micronutrients in Fungicide Applications*. HS1159. Gainesville: University of Florida Institute of Food and Agricultural Sciences. http://edis.ifas.ufl.edu/hs1159.

Sekhon, B. S. 2003. "Chelates for Micronutrient Nutrition among Crops." *Resonance* 8(7): 46–53. http://www.springerlink.com/content/8x4gr6850h346718/.

Schaffer, B., J. H. Crane, C. Li, Y. C. Li and E. A. Evans. 2011. "Re-Greening of Lychee (*Litchi chinensis* Sonn.) Leaves with Foliar Applications of Iron Sulfate and Weak Acids." *Journal of Plant Nutrition* 34(9): 1341–1359.

#### **Tables**

Table 1. Common synthetic and natural chelate compounds (ligands)

Abbreviation	Name	Formula	
CDTA	Cyclohexanediaminepentaacetic acid	C <sub>14</sub> H <sub>22</sub> O <sub>8</sub> N <sub>2</sub>	
CIT	Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	
DTPA	Diethylenetriaminepentaacetic acid	C <sub>14</sub> H <sub>23</sub> O <sub>10</sub> N <sub>3</sub>	
EDDHA	Ethylenediaminediaminedi-o-hydroxyphenylacetic acid	C <sub>18</sub> H <sub>20</sub> O <sub>6</sub> N <sub>2</sub>	
EDTA	Ethylenediamintetraacetic acid	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub> N <sub>2</sub>	
EGTA	Ethylene glycol bis(2-aminoethyl ether) tetraacetic acid	C <sub>14</sub> H <sub>24</sub> O <sub>10</sub> N <sub>2</sub>	
HEDTA	Hydroxyethylenediaminetriacetic acid	C <sub>10</sub> H <sub>18</sub> O <sub>7</sub> N <sub>2</sub>	
NTA	Nitrilo-triacetic acid	C <sub>6</sub> H <sub>9</sub> O <sub>6</sub> N	
ох	Oxalic acid	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	
PPA	Pyrophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	
TPA	Triphosphoric acid	H <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	
(Source: Havlin et al. 2005; Sekhon 2003)			

Table 2. Selected vegetable and fruit crop species' relative susceptibility\* to some micronutrient deficiencies

	Cu	Fe	Mn	Zn
Vegetable				
Asparagus Medium Low				

Bean	Low	High	High	High
Broccoli	Medium	High	Medium	
Cabbage	Medium	Medium	Medium	Medium
Cauliflower	Medium	High	Medium	
Carrot	High		Medium	Low
Celery	Medium		Medium	
Cucumber	Medium		High	
Lettuce	High		High	Medium
Mustard/crucifers				Low
Onion	High		High	
Pea	Low/medium	Medium	High	Low
Potato	Low	Low	High	Medium
Radish	Medium		High	
Spinach	High	High	High	Medium
Sweet corn	Medium	Medium	Medium	High
Tomato	Medium	High	Medium	Medium
Turnip	Medium			
Fruit				
Apple	Medium		High	High
Deciduous	Medium	High	High	High
Citrus	High	High	High	High
Grape	Medium	High	High	High

Raspberry		High	High	
Strawberry	Medium	High	High	

<sup>\*</sup> The high category needs micronutrient fertilization; the medium category probably needs fertilization; the low category usually does not need fertilization.

*Note*: Cultivars often respond differently to low soil micronutrient conditions. Check with your seed or transplant supplier about the attributes when selecting a cultivar source.

(Source: Alloway 2008; Havlin et al. 2005)

Table 3. Soil pH and chelated fertilizer requirements in commercial crop production

Soil pH < 5.3	Soil pH ranges from 5.3 to 6.5	Soil pH > 6.5
No chelated fertilizers are needed.	Chelated fertilizers may be needed.	Chelated fertilizers are needed.

At soil pH 5.3 or lower, soil can generally provide sufficient Fe, Cu, Mn, and Zn. In the soil pH range from 5.3 to 6.5, highly susceptible crop species may need chelated fertilizers. At soil pH 6.5 or greater, most crops need chelated fertilizers.

Table 4. Chelated fertilizers, formula, and nutrient content (%)

Source	Formula	Nutrient (w/w, %)
Iron chelates	NaFeEDTA	5-14
	NaFeEDDHA	6
	NaFeDTPA	10
Copper chelates	Na <sub>2</sub> CuEDTA	13 Cu
	Na <sub>2</sub> CuHEDTA	9
Manganese chelates	Na <sub>2</sub> MnEDTA	5-12 Mn
Zinc chelates	Na <sub>2</sub> ZnEDTA	14 Zn
	Na <sub>2</sub> ZnHEDTA	9-13 Zn
Natural organic materials	-	5-10 Fe, 0.5 Cu, 0.2 Mn, 1-5 Zn

Table 5. Examples of chelated fertilization rates for selected commercial vegetable and fruit crops

Crop	Nutrient Rate	Source
Iron:		
Vegetables	0.5–1 lb./100 gal. water/A	Iron chelates
Deciduous fruits	0.1–0.2 lb./25 gal. water/A	Iron chelates
Citrus	0.03–0.05 lb./2–5 gal. water/tree	Iron chelates
Copper:		
Corn	0.8 lb./100gal. water/A	Na <sub>2</sub> CuEDTA
Manganese:		
Vegetables	0.2–0.5 lb./200 gal. water/A	Na <sub>2</sub> MnEDTA
Zinc:		
Pecan	0.3–0.5 lb. Zn/100 gal. water/A	Na <sub>2</sub> ZnEDTA
(Source: Havlin et al. 2005)		1

#### **Footnotes**

- 1. This document is HS1208, one of a series of the Horticultural Sciences Department, UF/IFAS Extension. Original publication date November 2012. Revised September 2015. Visit the EDIS website at http://edis.ifas.ufl.edu.
- 2. Guodong Liu, assistant professor, Horticultural Sciences Department; Edward Hanlon, professor emeritus; and Yuncong Li, professor, Soil and Water Science Department; UF/IFAS Extension, Gainesville, FL 32611.

The Institute of Food and Agricultural Sciences (IFAS) is an Equal Opportunity Institution authorized to provide research, educational information and other services only to individuals and institutions that function with non-discrimination with respect to race, creed, color, religion, age, disability, sex, sexual orientation, marital status, national origin, political opinions or affiliations. For more information on obtaining other UF/IFAS Extension publications, contact your county's UF/IFAS Extension office.

U.S. Department of Agriculture, UF/IFAS Extension Service, University of Florida, IFAS, Florida A & M University Cooperative Extension Program, and Boards of County Commissioners Cooperating. Nick T. Place, dean for UF/IFAS Extension.

Copyright 2015 | Site Feedback | About This Site





Soil Biology & Biochemistry

www.elsevier.com/locate/soilbio

Soil Biology & Biochemistry 34 (2002) 1527-1536

#### Review

## Physiological effects of humic substances on higher plants

Serenella Nardi<sup>a,\*</sup>, Diego Pizzeghello<sup>a</sup>, Adele Muscolo<sup>b</sup>, Angelo Vianello<sup>c</sup>

<sup>a</sup>Dipartimento di Biotecnologie Agrarie, Agripolis, Università di Padova, Strada Romea 16, 35020 Legnaro, Padova, Italy <sup>b</sup>Dipartimento di Agrochimica ed Agrobiologia, Università di Reggio Calabria, Piazza S. Francesco 4, 89061 Gallina di Reggio Calabria, Italy <sup>c</sup>Dipartimento di Biologia ed Economia Agro-industriale, Sezione di Biologia Vegetale, Università di Udine, Via Cotonificio 108, 33100 Udine, Italy

Received 16 July 2001; received in revised form 15 July 2002; accepted 19 August 2002

#### **Abstract**

The physiological effects of humic substances (HS) on some aspects of plant growth and metabolism are examined. Evidence has been presented on that the effect of HS on plant growth depends on the source, concentration and molecular weight humic fraction. While a low molecular size (LMS < 3500 Da) fraction easily reaches the plasmalemma of higher plant cells and, in part, is taken up into them, a high molecular size fraction (HMS > 3500 Da) is not absorbed and can interact only with the cell wall. Therefore, a LMS fraction is the major candidate for determining the positive effects of HS on plant growth. The latter effects are in part exerted at the level of the plasma membrane by positively influencing the uptake of some nutrients, and in particular that of nitrate. The effects on the intermediary metabolism are less understood, albeit it seems that HS may influence both respiration and photosynthesis. Humic matter appears also to display an hormone-like activity. It is not clear if this activity is strictly linked to the chemical structure of HS or whether it depends on hormones of microbial origin entrapped into them. In any case, HS exhibit stimulatory effects on plant cell growth and development. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Humic matter; Chemical characteristics; Hormone-like activity; Intermediary metabolism; Ion uptake; Plant cells

#### 1. Introduction

Humic substances (HS), the major component of soil organic matter, are the subject of study in various areas of agriculture, such as soil chemistry, fertility, plant physiology as well as environmental sciences, because of the multiple roles played by these materials that can greatly benefit plant growth (Tan, 1998).

The beneficial effects of HS on plant growth may be related to their indirect (increase of fertilizer efficiency or reducing soil compaction), or direct (improvement of the overall plant biomass) effects. In particular, the increase of root growth is generally more apparent than that of the shoot (Vaughan and Malcom, 1985). The stimulatory effects of HS have been correlated to the maintenance of Fe and Zn in solution at effective concentrations (Clapp et al., 2001). In this context, HS have been widely regarded as playing a beneficial role in Fe acquisition by plants (Chen and Aviad, 1990; Pinton et al., 1999b). This effect has been mainly attributed to the complexing properties of HS, which

increase the availability of micronutrients from sparingly soluble hydroxides (Stevenson, 1991). Although only in part, HS, in particular those with a low molecular mass, are taken up by plants and, therefore, may also actively modify the plant metabolism (Vaughan and Malcom, 1985; Muscolo and Nardi, 1999). Their effects appear to be mainly exerted on cell membrane functions, promoting nutrient uptake (Visser, 1986; Varanini and Pinton, 1995), or plant growth and development, by acting as hormone-like substances (Vaughan and Malcom, 1985; Nardi et al., 1996).

This issue has been examined in recent reviews (Clapp et al., 2001; Varanini and Pinton, 2001). Therefore, this paper aims to reassess some physiological effects of HS on higher plant cells.

#### 2. Chemical characterization of humic matter

Many of the most important functions of HS will remain obscure, until the nature of these substances will not be elucidated. It is known that the chemical composition of humic matter includes many aromatic rings that interact

<sup>\*</sup> Corresponding author. Tel.: +39-49-8272905; fax: +39-49-8272929. *E-mail address*: serenella.nardi@unipd.it (S. Nardi).

with each other and with aliphatic chains, giving rise to macromolecules with different masses. Considering that the genesis of HS involves combinations of several reaction pathways and a wide variety of chemical binding systems, it is very difficult to define a clear concept on their composition (Hayes, 1997). Many of the original classical methods to understand the nature of HS were based on elemental composition, but the results obtained represent averages for agglomerations of molecules and it is impossible to derive precise empirical formulae from these data (Hayes et al., 1989).

Later, valuable information was gained from chemical degradation techniques (acid/base catalyzed hydrolysis, oxidative and reductive processes and thermal procedures), involving possible chemical constituents and building blocks of HS (Hayes, 1997). However, because the major linkages in the 'core' of HS are not hydrolysable, the energy inputs needed to cleave the links between the component molecules give rise to products that can be vastly different from the molecules that compose the macromolecules.

Considerable progress has been made in the last few years in providing an awareness of some of the gross features of HS (Hayes et al., 1989; Stevenson, 1994), by employing various spectroscopic procedures (Preston, 1996). Infrared spectroscopy has been the most widely used for studies of HS (MacCarthy and Rice, 1985), but the overlapping and the uncertainty of the assignations remain. Other approaches, which include electron spin resonance (Senesi and Steelink, 1989), Raman, ultraviolet—visible, fluorescence, X-ray photoelectron spectroscopy, have also been used.

The surface enhanced Raman spectroscopy technique has recently been employed (Francioso et al., 1996). Since its discovery, surface-enhanced Raman spectroscopy and surface-enhanced resonance Raman spectroscopy had been largely applied to the study of humic materials, demonstrating that it is possible to gather valuable information about the aromatic groups and the special conformation of these macromolecules in aqueous solution. The combined use of these techniques has shown an increase of oxygenated groups in HS with low molecular masses (Francioso et al., 1996).

In recent years, with the aim of studying HS, considerable effort has been focused on applications of solution- and solid-state <sup>13</sup>C NMR (nuclear magnetic resonance) spectroscopy to studies of HS composition. This technique has demonstrated that aliphatic compositions in HS are often as important or, occasionally, more important than aromatic structures. Aromaticity of HS, extracted from soils of differing pedological origins, ranges from 30 to 60%, with many in the 47–60% range. A substantial portion of aliphatic C in HS consists of paraffinic C. One of the advantages of <sup>13</sup>C NMR is that it indicates the presence in HS of a variety of structures whose determinations by others methods would either be laborious and time-consuming, or not possible at all. Even more valuable information on

the chemical nature HS can be obtained in an integrated approach by combining <sup>13</sup>C NMR with chemical and mass spectrometric methods. Of considerable interest is a comparison of solid-state <sup>13</sup>C NMR data of humic acids (HA) and fulvic acids (FA), extracted, respectively, from a Mollisol Ah horizon and from a Haplaquod Bh horizon (Table 1) (Schnitzer and Schulten, 1998). The spectra are divided into the following regions: 0-40 ppm (C in the straight-chain, branched, and cyclic aliphatics); 41–60 ppm (C in branched aliphatic, amino acids, and OCH<sub>3</sub> groups); 61-105 ppm (C in carbohydrates, and in aliphatic containing C bounded to OH, ether oxygens, or occurring in five- or six-membered rings bonded to O); 105-150 ppm (aromatic C), 151–170 ppm (phenolic C), and 171–190 ppm (C in CO<sub>2</sub>H groups). The main differences between HA and FA concern the following aspects: C distribution in the two humic fractions; HA are slightly more aromatic than FA, but the FA are considerably richer in CO<sub>2</sub>H groups; HA are richer in paraffinic C, but poorer in the carbohydrate-C than FA. Nevertheless, on the whole, the main features, such as aromaticity and aliphaticity are similar.

#### 3. Uptake of humic matter

The assertion that HS can have a direct effect on plant metabolism, implies that these substances are taken up into plant tissues (Vaughan and Malcom, 1985). Earlier work relied on color changes in plant organs as an indication of uptake (Prat, 1963). Later, isotopes of carbon were used, particularly <sup>14</sup>C-labeled HS (Vaughan and Ord, 1981; Vaughan, 1986). Vaughan (1986), using excised (25–35 mm long) roots from 2 d-old peas (*Pisum sativum*) found that the amount of radioactivity associated with roots increased with the concentration of HA and FA (Table 2). At all the concentrations used in the incubation media, FA were absorbed more than HA. When pea roots were

Table 1 Distribution of C (%) in a Mollisol humic acid (HA) and a Haplaquod fulvic acid (FA), determined by <sup>13</sup>C NMR (modified from Schnitzer and Schulten (1998))

	% of C		
Chemical shift range (ppm)	НА	FA	
0-40	24.0	15.6	
41-60	12.5	12.8	
61-105	13.5	19.3	
106-150	35.0	30.3	
151-170	4.5	3.7	
171-190	10.5	18.3	
Aliphatic C (0–105 ppm)	50.0	47.7	
Aromatic C (106–150 ppm)	39.5	34.0	
Phenolic C (151–170)	4.5	3.7	
Aromaticity <sup>a</sup>	44.1	41.6	

 $<sup>^{\</sup>rm a}$  ((aromatic C + phenolic C)/(aromatic C + phenolic C + aliphatic C))  $\times$  100.

Table 2 Incorporation of radioactivity by pea roots treated with increasing of concentrations of <sup>14</sup>C humic (HA) and <sup>14</sup>C fulvic acids (FA) (modified from Vaughan (1986))

Humic concentration	HA (μg <sup>14</sup> C 100	FA (μg <sup>14</sup> C 100
$(\text{mg l}^-1)$	mg l <sup>-1</sup> tissue)	mg l <sup>-1</sup> tissue)
10	43	58
25	73	117
50	124	197
100	193	290
150	233	352
200	252	398
250	298	413

incubated in labeled humus at different temperatures and in different experimental conditions (Tables 3 and 4), two uptake components were operating, the first was an initial and rapid passive process, while the second was a slower, but continuous, active uptake dependent on metabolism. Other data indicate that the initial uptake of HS is mainly confined to the cell wall (Vaughan, 1986). In agreement with the latter results, the different treatments (chelation with EDTA, pronase treatment or NaOH wash), used to remove the bound activity, had little effect. This indicates that almost all the labeled HS were tightly bound to the cell wall (Vaughan, 1986).

Further investigations on the uptake by plant roots of humic fractions, with different molecular masses, have supplied new insights. When pea roots were cultured at metabolic temperatures, in the presence of radioactive LMS fractions, the humic matter was taken up to a greater extent. In addition, it was found that 70% of the radioactivity was present in the supernatant fraction of pea roots. This was in contrast with the value of 25% recovered in the supernatant for the radioactive HMS humic fraction. When pea roots were cultured at low temperatures and in the presence of the two-labeled humic fractions, only the HMS fraction was absorbed by pea roots. These results support the interpretation that HS of all molecular weights can be absorbed and

Table 3
Uptake of <sup>14</sup>C humic acid (HA) by pea roots after 3, 6, 12, 18 h in different experimental conditions (modified from Vaughan (1986))

Root treatment	3 h $(\mu g^{14}C$ $100 \text{ mg } 1^{-1}$ tissue)	6 h (µg <sup>14</sup> C 100 mg l <sup>-1</sup> tissue)	12 h (µg <sup>14</sup> C 100 mg 1 <sup>-1</sup> tissue)	$^{18 \text{ h}}$ (µg $^{14}$ C $^{100 \text{ mg l}^{-1}}$ tissue)
Living (25 °C)	69	122	160	179
Living (4 °C)	41	49	56	65
Dead (25 °C)	35	42	37	43
Living (25 °C) plus2.5 µg ml <sup>-1</sup> CHM	48	87	195	117

Table 4
Uptake of <sup>14</sup>C humic acid (HA) and fulvic acid (FA) by pea roots after 1, 4, 18 h (modified from Vaughan, (1986))

Humic fraction	1 h (μg <sup>14</sup> C 100 mg 1 <sup>-1</sup> tissue)	4 h (μg <sup>14</sup> C 100 mg l <sup>-1</sup> tissue)	18 h ( $\mu$ g <sup>14</sup> C 100 mg l <sup>-1</sup> tissue)
НА	54	83	134
HA water insoluble	49	81	122
HA water soluble	34	94	223
FA	31	89	231

show evidence that the uptake of LMS is dependent on the active component of transport (Vaughan, 1986). The LMS fraction absorbed by roots was then transferred to the shoots, but, even in these cases, the amount transferred was not higher than 10–12% (Vaughan, 1986). This pattern has been confirmed by Muscolo and Nardi (1999), utilizing LMS and HMS fractions conjugated with fluorescein isothiocianate (FITC). They showed that only the LMS humic fraction was able to interact with the plasma membrane of cultured carrot cells.

#### 4. Role of the humic matter in the ion absorption

The influence of soil humus on ion uptake, and more in general on plant growth, has been examined by Vaughan and Malcom (1985), Chen and Aviad (1990), Varanini and Pinton (2001) and Clapp et al. (2001). The effects of HS on ion uptake appear to be more or less selective and variable, in relation to their concentration and to the pH of the medium. In beetroot disks, HA stimulated the development of an uptake capacity for Na+, Ba2+, while that of Ca2+ and Zn2+ were unaffected (Vaughan and MacDonald, 1976). This fraction also enhanced the development of phosphate uptake capacity, but retarded that of chloride (Vaughan and MacDonald, 1971). The development of the Na uptake capacity was related to protein synthesis, because cycloheximide and D-threo-chloramphenicol (two protein synthesis inhibitors) inhibited it. However, HA were not able to overcome this inhibitory effect and did not affect the incorporation and distribution of <sup>14</sup>C-labeled amino acids into proteins (Vaughan and MacDonald, 1976). In addition, it has been reported that HMS and LMS fractions (Albuzio et al., 1986) and HA and FA may affect NO<sub>3</sub>, SO<sub>4</sub><sup>2</sup> and K+ uptake by barley and oat seedlings (Maggioni et al., 1987). The most prominent stimulatory effect concerns NO<sub>3</sub> uptake in oat roots, although this was evident only after several hours of exposure (Nardi et al., 1991).

The effects of HS on ion absorption by plant roots are not easily explainable, owing to the complex and still unknown nature of these substances. Furthermore, the effects described in these papers are difficult to compare, because HS with different features (due to the origin of the soil and

the methods of extraction) were assayed. It is possible that HS may exert several effects on plant functions and that some of these may result, directly or indirectly, in a modulation of ion uptake. In this scenario, a first line of evidence is based on experiments carried out by utilizing both transcription (6-methylpurine) and translation (cycloheximide) inhibitors. It has been shown that HA stimulated carrier-protein synthesis in barley roots at a post-transcriptional level (Dell'Agnola and Ferrari, 1971; Dell'Agnola et al., 1981). This conclusion has been recently confirmed by determining the messenger RNA amount, after treatment of maize seedlings with LMS fraction (Nardi et al., 2000b). The analysis of the synthesized polypeptides revealed a post-transcriptional effect of humic matter on protein synthesis and, consequently, on the overall plant nutrition machinery. However, doubts remain concerning the exact step in which these substances could exert their effects. In any case this mechanism is in line with both relatively old and recent findings, showing that HS (HMS and LMS fractions) stimulated NO<sub>3</sub> by promoting the expression of nitrate carrier proteins (Vaughan et al., 1985), and which also resulted in the modification of some kinetic parameters (Cacco et al., 2000). But the effects of HMS and LMS fractions on NO<sub>3</sub> uptake could also be explained by considering that these substances may act as hormone-like substances (Cacco and Dell'Agnola, 1984; Dell'Agnola and Nardi, 1987; Nardi et al., 1988), or that they induce genome modifications (Attinà et al., 1992). In particular, it has been shown by Nardi et al. (2000b) that only LMS fraction, endowed with gibberellin-like activity, could increase NO<sub>3</sub> uptake, while they strongly inhibited microsomal ATPase activity and H<sup>+</sup> extrusion by roots, in the same way as when gibberellic acid was used. In any case, the mechanisms suggested can explain why the stimulatory effects of LMS fraction on NO<sub>3</sub> uptake required long periods of incubation through a regulation of the 'coarse' type.

As it is known, primary active transport by plant cells depends on the presence of a vanadate-sensitive protonpumping ATPase (H<sup>+</sup>-ATPase) that builds up an electrochemical proton gradient across the plasma membrane (Morsomme and Boutry, 2000). The latter energizes secondary active transport, accomplished by carrier proteins via symport or antiport. In this context, NO<sub>3</sub> is taken up by an inducible H<sup>+</sup>/NO<sub>3</sub> symport with a stoichiometry of 2:1 (Miller and Smith, 1996). Another line of evidence supports the hypothesis that LMS fraction could interact with these transport proteins ('fine' regulation), leading to modulation of NO<sub>3</sub> uptake. This contention is reinforced by the observation that LMS fraction can reach the apoplast and interact with the plasma membrane of roots (Vaughan, 1986) and cultured carrot cells (Muscolo and Nardi, 1999). The first evidence for an effect of HS on transport proteins concerns the stimulation caused by HMS and LMS fractions on the activity of the K<sup>+</sup>-stimulated ATPase (believed to be coincident with the H<sup>+</sup>-ATPase of plasma membranes) of microsomal fractions (Maggioni et al., 1987; Nardi et al., 1991; Pinton et al., 1992). Similar results were also obtained by showing that HA stimulated proton extrusion by roots in a vanadate-sensitive manner, although this increase was apparent only after 2–4 h of incubation (Pinton et al., 1997). Nevertheless, this effect has been interpreted as a consequence of a direct stimulation of HA on the proton pump (H<sup>+</sup>-ATPase). LMS fraction could also stimulate the H<sup>+</sup>-ATPase activity of isolated plasma membranes (Varanini et al., 1993), thus determining an increase of the electrochemical proton gradient which might be, at least in part, responsible for the stimulation of NO<sub>3</sub> uptake (Pinton et al., 1999a).

Finally, owing to their polyanionic (acid) nature, HS could simply act as surface-active molecules (Visser, 1986; Nardi et al., 1991). By decreasing the pH at the surface of the plasma membranes of root cells, HS may counteract the alkalinization which occurs when  $NO_3^-$  is used as a N source and that is responsible for inhibiting the  $H^+/NO_3^-$  symport (Raven and Smith, 1976). Concordantly, when there was a decrease of  $NO_3^-$  uptake, at the same time, an increase in the  $NH_4^+$  uptake takes place (Barber, 1984).

The plasma membranes of plant cells possess several redox activities that can be related to both plant nutrition and cell wall formation and lignification (Lüthje et al., 1997; Bérczi and Møller, 2000). In this context, it has been shown that, in oat roots, HMS humic fractions inhibited NADH oxidation in either the presence or absence of an artificial electron acceptor (ferricyanide), whereas LMS fractions inhibited this oxidase only if the electron donor (NADH) and acceptor (ferricyanide) were contemporarily added (Pinton et al., 1995). While the first effect could be related to the activity of surface peroxidases that can be involved in cell wall formation and thickening (Vianello and Macrì, 1991), the second seems to be exerted on a different redox system with an unknown function.

It is well known that Fe absorption by roots of dicotyledonous plants requires a preliminary reduction of Fe(III) to Fe(II) by a Fe(III)-chelate reductase of plasma membranes (Moog and Brüggemann, 1994). It has been shown that Fe-deficient cucumber plants, at least in part, could use Fe complexed with HS to reduce Fe(III) before being absorbed by the roots (Pinton et al., 1998; Pinton et al., 1999b).

#### 5. Effect of humic matter on intermediary metabolism

A first aspect concerns the effect of HS on respiration, although it is poorly understood. Our knowledge is mainly based on results that have already been critically examined in some reviews (Vaughan and Malcom, 1985; Chen and Aviad, 1990; Varanini and Pinton, 1995; Nardi et al., 1996). Surprisingly, the effect of HS on respiration of plant cells, despite its relevance, has received little attention in recent

years. Therefore, in this section we only reassess this issue in the light of our more recent progresses on this aspect of plant cell physiology (Affourtit et al., 2001).

There are many reports showing that HS, extracted from a wide range of soils, were able to enhance respiration of higher plants (Vaughan and Malcom, 1985), with the effects of FA more pronounced than that of HA. These results have been interpreted in varying ways. The possibility that HSinduced stimulation can depend on the property of these substances to act as substrates or respiratory chain catalysts is no longer acceptable. In addition, the stimulation of O<sub>2</sub> consumption is only in the order of 25–30% and obtained with intact plants, such as tomato (Sladky, 1959) or beet slices (Vaughan, 1967a). But this increase could also be linked to a stimulation of peroxidase activity by HS (Muscolo et al., 1993). Indeed the latter activity implies an O<sub>2</sub> uptake, which is not distinguishable, at the tissue level, from that linked to respiration, being both cyanidesensitive.

This aspect has also been addressed by using isolated rat liver mitochondria. It has been shown that HS partially uncoupled oxidative phosphorylation after a short exposure (Visser, 1987). This effect can explain previous results showing that synthetic HS also uncoupled oxidative phosphorylation, thus decreasing ATP concentration. These partial uncoupling has been confirmed by using isolated higher plant mitochondria (Flaig, 1968), albeit this effect was also accompanied by an increase of dry matter and sometimes, as in cereals, of yield grain. This apparent contradictory results have been explained suggesting that the partial uncoupling renders some inorganic phosphate available, without depleting cellular ATP, which is then used in some phosphorylating reactions linked to biosynthetic pathways. However, it has been demonstrated that incubation of mitochondria with HS for a long period resulted in a positive influence on oxidative phosphorylation (Visser, 1987), a result that could explain the finding that HS caused an increase of ATP production (Khristeva et al., 1980). The latter observations are, however, difficult to reconcile with the former. In addition, more recent results show that HS determined a decrease (30-40%) of cellular ATP, without affecting O<sub>2</sub> consumption (Nardi et al., 1991).

From the above findings and considerations, it is not clear whether HS influence respiration by directly or indirectly interfering with mitochondria, thereby making new experimental work necessary prior to drawing a firmer conclusion.

A second aspect that has been examined concerns photosynthesis. Even in this case, our information is fragmentary and not very recent. Although indirect, the most prominent effect of HS application to growing plants was an increase of chlorophyll content which, in turn, could affect photosynthesis (Sladky, 1959). However, the increase of chlorophyll alone did not necessarily result in higher yields. HS, applied to the growth solution, stimulated enzyme activities related to the photosynthetic sulphate

reduction pathway (Ferretti et al., 1991). This positive effect of HS has also been observed on the main photosynthetic metabolism in maize leaves, where a decrease in starch content was accompanied by an increase of soluble sugars (Merlo et al., 1991). This change appeared to be mediated by variations of the activity of the main enzymes involved in carbohydrate metabolism.

#### 6. Hormone-like activity of HS

In a series of papers published between 1914 and 1920 (Bottomley, 1914a,b; 1917, 1920), Bottomley showed that HS enhanced plant growth by providing substances called 'auximones', a conclusion that has been independently and successively reached also by Hillitzer (1932) and Chaminade and Boucher (1940). Later, using isolated root tips from peas, O'Donnell (1973) concluded that HS exhibited an auxin-like activity, confirming a previous result obtained by Paszewski et al. (1957). These findings have been further supported and extended by showing that humic fractions have a high hormonal activity (Cacco and Dell'Agnola, 1984; Dell'Agnola and Nardi, 1987; Nardi et al., 1988; Piccolo et al., 1992).

In this context, new information arising from more recent papers has further supported this hypothesis. In particular, it has been shown that only LMS fractions induced morphological changes similar to those caused by indole-3-acetic acid (IAA) (Muscolo et al., 1993). In addition, the LMS fraction increased both peroxidase and IAA oxidase activity, albeit IAA increased IAA oxidase, but inhibited peroxidase activity. Again, Nardi et al. (1994), utilizing two inhibitors of auxin (TIBA, 2,3,5-triiodobenzoic acid and PCIB, 4-chlorophenoxy-isobutyric acid), demonstrated that the IAA and LMS fractions induced root growth of Nicotiana plumbaginifolia, while TIBA or PCIB alone inhibited it. The presence of TIBA plus LMS fractions or TIBA plus IAA inhibited root growth, while explants, grown in the presence of IAA plus PCIB or LMS fractions plus PCIB, showed roots similar to those obtained with IAA or LMS fractions, respectively. These results thus confirm that the LMS component of humic matter is the fraction endowed with auxin-like activity, although the pathways followed by the IAA and the LMS fraction in inducing their effects may be somewhat different (Fig. 1).

In an attempt to evaluate the possible interaction of the LMS fraction with plasma membranes (target of IAA) of carrot cells, Muscolo and Nardi (1999) labeled with fluorescein isothiocyanate (FITC) IAA, HMS and LMS. The results showed that fluorescent plasma membrane staining was only observed in IAA- and LMS fraction-treated cell cultures. Prior treatment of carrot cells with unconjugated IAA or LMS humic fractions blocked the fluorescein staining of both the FITC-IAA and FITC-LMS humic fraction, giving indirect evidence of the possible binding site of LMS humic

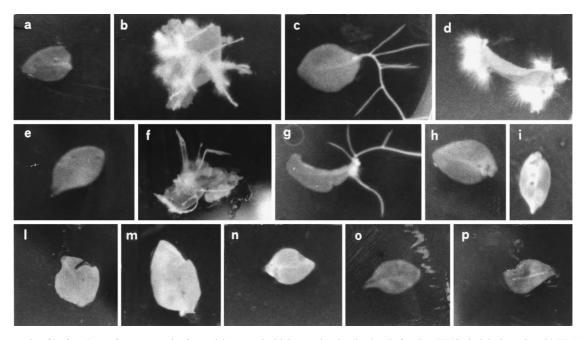


Fig. 1. Photographs of leaf explants of *Nicotiana plumbaginifolia* treated with low molecular size humic fraction (LMS), indole-3-acetic acid (IAA), inhibitors of IAA (TIBA, 2,3,5-triiodobenzoic acid and PCIB, 4-chlorophenoxy-isobutyric acid) and cycloheximide (a, control; b, IAA; c, LMS; d, IAA + LMS; e, PCIB; f, PCIB + IAA; g, PCIB + LMS; h, TIBA; i, TIBA + IAA; l, TIBA + LMS; m, PCIB + TIBA; n, cycloheximide; o, cycloheximide + IAA; p, cycloheximide + LMS).

fraction to the IAA cell membrane receptors (Fig. 2). It is important to emphasize that the interaction of HS with cellular membrane is not due to the possible presence of auxin components in this preparation. In fact, using different approaches, the IAA content was identified in the 0.5% (w/v) to 3.7% range in the LMS humic fraction, according to the different sensitivities of the assays and the methodology used (Muscolo et al., 1998). A recent result seems to corroborate the above findings (H. MacDonald, pers comm). She has shown that IAA and LMS fractions had the same effect on the stomatal opening in pea leaves. This inducing effect appears to be mediated by phospholipase A2 (PLA2) and protein kinase C (PKC), both enzymes involved in the signal transduction pathway leading to the response of plants to IAA (Scherer and Andre, 1989; Nemeth et al., 1998).

Very recently the hormone-like activity of humic matter has been questioned in favor of a major effect of these substances on the plasma membrane H<sup>+</sup>-ATPase (Varanini and Pinton, 2001), or on an increased availability of microelements (Fe and Zn) (Clapp et al., 2001). These conclusions appear, however, somewhat simplistic and do not consider the very complex nature of HS.

It is known that different soils vary in their native auxin content (Hamence, 1946) and fertile soils contain greater amounts of auxins than those that are less fertile (Stewart and Anderson, 1942; Dahm et al., 1977). Auxin and gibberellin concentrations are usually higher in the rhizosphere than in the bulk soil, probably as a consequence of increased microbial populations or of an accelerated

metabolism owing to the presence of root exudates. Although numerous soil and rhizosphere micro-organisms, as well as the root systems of higher plants have been reported to produce auxins (Lebuhn and Hartmann, 1993) and gibberellins (Rademacher, 1992), there is little information about their stability. Therefore, only indirect conclusions have been drawn about their presence in amounts high enough to be biologically-active (Frankenberger and Arshad, 1995). Perhaps, HS could be considered as a sort of memory of microbial population and plant cover. Frankenberger and Arshad (1995) have found that the active ingredients in humus were not mineral nutrients, but were organic substances and biologically-active metabolites of various microbes. Indeed, mineral substances applied in equal amounts to soil had little effects on plant growth. The favorable effects of organic substances were observed primarily after decomposition and processing of humus, compost, and peat. Biological and biochemical transformations are most likely to occur upon degradation of these materials. This implies that the biologically active substances of humus are not the original parent compounds, but are products of microbial metabolism. The starting organic materials may comprise compounds that serve as precursors or as substrates for the synthesis of biologically active substances, including hormone-like substances, by the heterotrophic activity of the soil microbiota. These plant growth regulators, kept within HS, are of ecological importance because they do not leach and, at the same time, become available for plants (Nardi et al., 2000a; Pizzeghello et al., 2001).

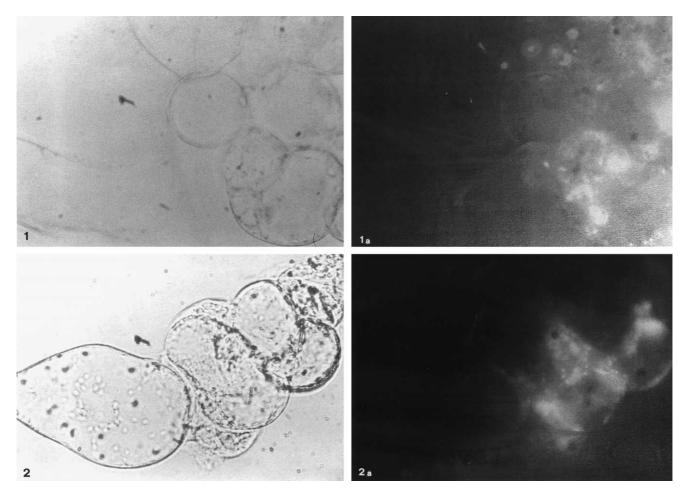


Fig. 2. Light (1 and 2) and fluorescence (1a and 2a) microscopy of carrot cells incubated with fluorescein isothiocyanate FITC-HMS (high molecular size) (1 and 1a) and FITC-LMS (2 and 2a) humic fractions.

#### 7. Structure–activity relationships of HS

The lack of detailed knowledge on the composition of HS renders makes it very difficult to identify the relationships between the structure and the activity of these substances. The study of these relationships is complicated, as seen above, by the presence of other molecules, such as hormones of microbial origin. Thus, attempts to relate these two aspects have produced conflicting results. Nevertheless, it has been suggested that functional carboxylic and hydroxylic groups of HS could play a major role in determining their activity (Mato et al., 1972; Malcom and Vaughan, 1978; Pflug and Ziechmann, 1981), but the manner by which they exert their effects remains to be elucidated (Vaughan and Malcom, 1985). Low molecular weight components of HS were shown to be particularly active (Vaughan, 1967a,b, Mato et al., 1972; Vaughan et al., 1974), although high molecular mass components had a residual activity (Ladd and Butler, 1971; Malcom and Vaughan, 1979). The effectiveness of LMS fractions was due to a combination of the low molecular weight and the high content of aromatic, carboxylic and phenolic groups (Piccolo et al., 1992; Nardi et al., 1998,

2000a,b). This aspect has already been described by Visser (1986), who noticed that LMS fractions and FA possessed a higher metal binding capability with respect to HMS fractions, because of the larger number of functional groups (in particular carboxylic and phenolic OH groups). This could explain how they improve nutrient assimilation and plant metabolism. Moreover, LMS humus complexes entered cells more easily then their HMS counterparts. High molecular mass humic fractions could have an opposite effect in plants, promoting the plant growth, but decreasing enzyme activity (Visser, 1986; Nardi et al., 1988). In any case, HMS substances have been reported to be irreversibly fixed on the external cell surface (Vaughan and Ord, 1981) and, as previously described, the majority of HMS fraction was tightly bound to the cell wall (Vaughan, 1986). These results are in line with those of Nardi et al. (1996, 2000a), who showed that HMS humus treatment induced a higher rate of root differentiation and the stimulation of enzyme activities in metabolic processes related to plant growth and differentiation. Again, Sessi et al. (2002) showed that LMS fractions greatly stimulated NO<sub>3</sub> uptake, while HMS substances required a long period of exposure in NO<sub>3</sub>

medium in order to exhibit a low stimulation. This result agrees with that Vaughan (1986) obtained, who demonstrated that only 25% of the radioactivity of HMS substances remained in the supernatant of pea root seedlings which had been incubated in HMS humus radioactive solution.

Such observations indicate that the LMS fraction, which is endowed with a high aromatic, carboxylic and phenolic C and with a low molecular weight, acts at the symplast and directly influences plant metabolism. One idea is that HMS fraction operates mainly on the cell wall influencing the differentiation and growth process at the apoplast. Clearly, more work is required in this important area of plant nutrition.

#### 8. Conclusions

It is clear from the above that HS may positively influence higher plant metabolism. This function seems to be carried out more readily by LMS humic fractions, because they are able to reach the plasma membrane of root cells and then to be translocated. Unfortunately, the as yet unknown nature of HS prevents us from drawing more conclusive results concerning the effects of HS on plant growth. We can only affirm that HS appear to influence the metabolism of plant cells at different levels. Their effects may, therefore, be different and be additive, overlapping, or, in some cases, mechanistic related. This apparently puzzling situation can be however, rationalized by hypothesizing that HS have several targets that can be explained partly by their chelating capacity and partly by their hormone-like activity. This is not surprising, considering the complex and differentiated nature of HS. Therefore, more research is necessary to explain the positive effects of HS on higher plants. In particular these studies have to be, primarily, focused on the following topics: (1) the availability of humus in the soil solution and in the rhizosphere; (2) the link between humus activity and the presence in the soil solution of active metabolites of various microbes; and (3) the use of more characterized HS in experiments on plant metabolism.

#### References

- Affourtit, C., Krab, K., Moore, A.L., 2001. Control of plant mitochondrial respiration. Biochimica Biophysica Acta 1504, 58–69.
- Albuzio, A., Ferrari, G., Nardi, S., 1986. Effects of humic substances on nitrate uptake and assimilation in barley seedlings. Canadian Journal of Soil Science 66, 731–736.
- Attinà, E., Nostro, G., Sidari, M., Cacco, G., 1992. Changes in gene structure and its expression induced by humic substances in plant tissues. First Workshop of International Soil Science Society, Working Group, MO, Canada, pp. 11–15.
- Barber, S.A., 1984. Soil Nutrient Bioavailability. A Mechanistic Approach, Wiley-Interscience, New York, 194 p.

- Bérczi, A., Møller, I.M., 2000. Redox enzymes in the plant plasma membrane and their possible roles. Plant Cell and Environment 23, 1287-1302.
- Bottomley, W.B., 1914a. Some accessory factors in plant growth and nutrition. Proceedings of the Royal Society of London (Biology) 88, 237–247.
- Bottomley, W.B., 1914b. The significance of certain food substances for plant growth. Annals of Botany, (London) 28, 531–540.
- Bottomley, W.B., 1917. Some effects of organic growth-promotion substances (auximones) on the growth of *Lemma minor* in mineral cultural solutions. Proceedings of the Royal Society of London (Biology) 89, 481–505.
- Bottomley, W.B., 1920. The effect of organic matter on the growth of various plants in culture solutions. Annals of Botany, (London) 34, 353–365.
- Cacco, G., Dell'Agnola, G., 1984. Plant growth regulator activity of soluble humic complex. Canadian Journal of Soil Science 62, 306–310.
- Cacco, G., Attinà, E., Gelsomino, A., Sidari, M., 2000. Effect of nitrate and humic substances of different molecular size on kinetic parameters of nitrate uptake in wheat seedlings. Journal of Plant Nutrition and Soil Science 163, 313–320.
- Chaminade, R., Boucher, I., 1940. Recherches sur la présence de substances rhizogenes dans certains milieux naturels. C.R. Séances Academiques Agriculture Francaises 26, 66.
- Chen, Y., Aviad, T., 1990. Effects of humic substances on plant growth. In: MacCarthy, P., Clapp, C.E., Malcom, R.L., Bloom, P.R. (Eds.), Humic Substances in Soils and Crop Science: Selected Readings, Soil Science Society of America, Madison, pp. 161–186.
- Clapp, C.E., Chen, Y., Hayes, M.H.B., Cheng, H.H., 2001. Plant growth promoting activity of humic substances. In: Swift, R.S., Sparks, K.M. (Eds.), Understanding and Managing Organic Matter in Soils, Sediments, and Waters, International Humic Science Society, Madison, pp. 243–255.
- Dahm, H., Sitek, J.M., Strzelczyk, E., 1977. Synthesis of auxins by bacterial isolated from the roots of pine seedlings inoculated with rusty forest soil. Polish Journal of Soil Science 10, 131–137.
- Dell'Agnola, G., Ferrari, G., 1971. Effect of humic acids on anion uptake by excised barley roots. Proceedings of the International Symposium Humus et Planta V. Prague, pp. 567–570.
- Dell'Agnola, G., Nardi, S., 1987. Hormone-like effect of enhanced nitrate uptake induced by depolycondensed humic fractions obtained from *Allolobophora rosea* and *A. caliginosa* faeces. Biology and Fertility of Soils 4, 115–118.
- Dell'Agnola, G., Ferrari, G., Nardi, S., 1981. Antidote action of humic substances on atrazine inhibition of sulphate uptake in barley roots. Pesticide Biochemistry and Physiology 15, 101–104.
- Ferretti, M., Ghisi, R., Nardi, S., Passera, C., 1991. Effect of humic substances on photosynthetic sulphate assimilation in maize seedlings. Canadian Journal of Soil Science 71, 239–242.
- Flaig, W., 1968. Uptake of organic substances from soil organic matter by plants, Study Week on Organic Matter and Soil Fertility, Wiley– Interscience, New York, pp. 723–776.
- Francioso, O., Sáncehez-Cortés, S., Tugnoli, V., Ciavatta, C., Sitti, L., Gessa, C., 1996. Infrared, Raman and nuclear magnetic resonance (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) spectroscopy in the study of fractions of peat humic acids. Applied Spectroscopy 50, 1165–1174.
- Frankenberger, W.T., Arshad, M., 1995. Phytohormones in Soils, Marcel Dekker, New York.
- Hamence, J.H., 1946. The determination of auxins in soils, including a note on synthetic growth substances. The Analyst 71, 111–116.
- Hayes, M.H.B., 1997. Emerging concepts of the compositions and structure of humic substances. In: Hayes, M.H.B., Wilson, W.S. (Eds.), Humic Substances in Soils, Peats and Waters—Health and Environmental Aspects, The Royal Society of Chemistry, Cambridge, pp. 3–30.
- Hayes, M.H.B., MacCarthy, P., Malcolm, R.L., Swift, R.S., 1989. Structures of humic substances, the emergence of forms. In: Hayes,

- M.H.B., MacCarthy, P., Malcolm, R.L., Swift, R.S. (Eds.), Humic Substances II. In Search of Structures, Wiley, Chichester, pp. 689–733.
- Hillitzer, A., 1932. Über den einfluss der humusstoffe auf das wurzelwachstum. Beihefte zum Botanischen Zentralblatt 49, 467–480.
- Khristeva, L.A., Gallushko, A.M., Gorovaya, A.I., Kolbassin, A.A., Shortshoi, L.P., Tkatshenko, L.K., Fot, L.W., Luk'Yakenko, N.V., 1980. The main aspects of using physiologically active substances of humus nature. VI International Peat Congress, Minnesota.
- Ladd, J.M., Butler, J.H.A., 1971. Inhibition and stimulation of proteolytic enzyme activities by soil humic acids. Australian Journal of Soil Research 7, 253–261.
- Lebuhn, M., Hartmann, A., 1993. Method for determination of indole-3-acetic acid and related compounds of L-tryptophan catabolism in soils. Journal of Chromatography 629, 255–266.
- Lüthje, S., Döring, O., Heuer, S., Lüthen, H., Böttger, M., 1997.
  Oxidoreductases in plant plasma membranes. Biochimica et Biophysica Acta 1331, 81–102.
- MacCarthy, P., Rice, J.A., 1985. Spectroscopic methods and other than NMR for determining functionality in humic substances. In: Aiken, G.R., McKnight, D.M., Wershaw, R.L., MacCarthy, P. (Eds.), Humic Substances in Soil Sediment and Water, Wiley-Interscience, New York, pp. 527–559.
- Maggioni, A., Varanini, Z., Nardi, S., Pinton, R., 1987. Action of soil humic matter on plant roots: stimulation of ion uptake and effects on (Mg<sup>2+</sup> K<sup>+</sup>) ATPase activity. Science of the Total Environment 62, 355–363.
- Malcom, R.E., Vaughan, D., 1978. Effects of humic acid fractions on invertase activities in plant tissues. Soil Biology & Biochemistry 11, 65-72.
- Malcom, R.E., Vaughan, D., 1979. Humic substances and phosphatase activities in plant tissues. Soil Biology & Biochemistry 11, 253–259.
- Mato, M.C., Olmedo, M.G., Mendez, J., 1972. Inhibition of indoleacetic acid-oxidase by soil humic acids fractionated on Sephadex. Soil Biology & Biochemistry 44, 69–473.
- Miller, A.J., Smith, S.J., 1996. Nitrate transport and compartmentation in cereal root cells. Journal of Experimental Botany 47, 843–854.
- Merlo, L., Ghisi, R., Rascio, N., Passera, C., 1991. Effects of humic substances on carbohydrate metabolism of maize leaves. Canadian Journal of Plant Science 71, 419–425.
- Moog, P.R., Brüggemann, W., 1994. Iron reductase systems on the plant plasma membrane—a review. Plant and Soil 165, 241–260.
- Morsomme, P., Boutry, M., 2000. The plant plasma membrane H+-ATPase: structure, function and regulation. Biochimica et Biophysica Acta 1465, 1–16.
- Muscolo, A., Nardi, S., 1999. Effetti di due frazioni umiche sul metabolismo azotato di cellule di Daucus carota. IV Convegno Nazionale dell' IHSS, Le ricerche di base e le applicazioni delle sostanze umiche alle soglie del 2000. Alghero, Italy, pp. 103–106.
- Muscolo, A., Felici, M., Concheri, G., Nardi, S., 1993. Effect of earthworm humic substances on esterase and peroxidase activity during growth of leaf explants of *Nicotiana plumbaginifolia*. Biology and Fertility of Soils 15, 127–131.
- Muscolo, A., Cutrupi, S., Nardi, S., 1998. IAA detection in humic substances. Soil Biology & Biochemistry 30, 1199–1201.
- Muscolo, A., Bovalo, F., Gionfriddo, F., Nardi, S., 1999. Earthworm humic matter produces auxin-like effects on *Daucus carota* cell growth and nitrate metabolism. Soil Biology & Biochemistry 31, 1303–1311.
- Nardi, S., Arnoldi, G., Dell'Agnola, G., 1988. Release of the hormone-like activities from *Allolobophora rosea* and *A. caliginosa* faeces. Canadian Journal of Soil Science 68, 563–567.
- Nardi, S., Concheri, G., Dell'Agnola, G., Scrimin, P., 1991. Nitrate uptake and ATPase activity in oat seedlings in the presence of two humic fractions. Soil Biology & Biochemistry 23, 833–836.
- Nardi, S., Panuccio, M.R., Abenavoli, M.R., Muscolo, A., 1994. Auxin-like effect of humic substances extracted from faeces of *Allolobo-phora caliginosa* and *A. rosea*. Soil Biology & Biochemistry 26, 1341–1346.

- Nardi, S., Concheri, G., Dell'Agnola, G., 1996. Biological activity of humic substances. In: Piccolo, A., (Ed.), Humic Substances in Terrestrial Ecosystems, Elsevier, Amsterdam, pp. 361–406.
- Nardi, S., Pizzeghello, D., Muscolo, A., Dalla Vecchia, F., Concheri, G., 1998. Effects of forest humus on biological activity in roots of *Pinus sylvestris* related to chemical humus fraction characteristics. Fresenius Environmental Bulletin 7, 203–208.
- Nardi, S., Pizzeghello, D., Reniero, F., Rascio, N., 2000a. Chemical and biochemical properties of humic substances isolated from forest soils and plant growth. Soil Science Society of America Journal 64, 639–645.
- Nardi, S., Pizzeghello, D., Gessa, C., Ferrarese, L., Trainotti, L., Casadoro, G., 2000b. A low molecular weight humic fraction on nitrate uptake and protein synthesis in maize seedlings. Soil Biology & Biochemistry 32, 415–419.
- Nemeth, K., Salchert, K., Putnoky, P., Bhalerao, R., Koncz-Kalman, Z., Stankovic-Stangeland, B., Bako, L., Mathur, J., Okresz, L., Stabel, S., Geigenberger, P., Stitt, M., Redei, G.P., Schell, J., Koncz, C., 1998. Pleiotropic control of glucose and hormone responses by PRL1, a nuclear WD protein, in *Arabidopsis*. Genes and Development 12, 3059–3073.
- O'Donnell, R.W., 1973. The auxin-like effects of humic preparations from leonardite. Soil Science 116, 106–112.
- Paszewski, A., Trojanowski, J., Lobarzewska, W., 1957. Influence of the humus fraction on the growth of oat coleoptiles. Annales Universitatis Marie Curie Sklodowska, Sklodowska 12, 1–13.
- Pflug, W., Ziechmann, W., 1981. Inhibition of malate dehydrogenase by humic acids. Soil Biology & Biochemistry 13, 293–299.
- Piccolo, A., Nardi, S., Concheri, G., 1992. Structural characteristics of humus and biological activity. Soil Biology & Biochemistry 24, 273–380.
- Pinton, R., Varanini, Z., Vizzotto, G., Maggioni, A., 1992. Soil humic substances affect transport properties of tonoplast vesicles isolated from oat roots. Plant and Soil 142, 203–210.
- Pinton, R., Cesco, S., Santi, S., Varanini, Z., 1995. Effect of soil humic substances on surface redox activity of oat roots. Journal of Plant Nutrition 18, 2111–2120.
- Pinton, R., Cesco, S., Santi, S., Varanini, Z., 1997. Soil humic substances stimulate proton release by intact oat seedling roots. Journal of Plant Nutrition 20, 857–869.
- Pinton, R., Cesco, S., De Nobili, M., Santi, S., Varanini, Z., 1998. Waterand pyrophosphate-extractable humic substances fractions as source of iron for Fe-deficient cucumber plants. Biology and Fertility of Soils 26, 23–27.
- Pinton, R., Cesco, S., Iacoletti, G., Astolfi, S., Varanini, Z., 1999a. Modulation of nitrate uptake by water-extractable humic substances: involvement of root plasma membrane H + -ATPase. Plant Soil 215, 155–163.
- Pinton, R., Cesco, S., Santi, S., Agnolon, F., Varanini, Z., 1999b. Water-extractable humic substances enhance iron deficiency responses by Fedeficient cucumber plants. Plant and Soil 210, 145–157.
- Pizzeghello, D., Nicolini, G., Nardi, S., 2001. Hormone-like activity of humic substances in *Fagus sylvatica* forests. New Phytologist 151, 647–657.
- Prat, S., 1963. Permeability of plant tissues to humic acids. Biologia Plantarum 5, 279–283.
- Preston, C.M., 1996. Applications of NMR to soil organic matter analysis: history and prospects. Soil Science 161, 44–166.
- Rademacher, W., 1992. Occurrence of gibberellins in different species of the fungal genera *Sphaceloma* and *Elsinoe*. Phytochemistry 31, 4155–4157.
- Raven, J.A., Smith, F.A., 1976. Nitrogen assimilation and transport in vascular land plants in relation to intracellular pH regulation. New Phytologist 76, 415–431.
- Scherer, G.F., Andre, B., 1989. A rapid response to a plant hormone: auxin stimulates phospholipase A<sub>2</sub> in vivo and in vitro. Biochemical and Biophysical Research Communications 163, 111–117.

- Schnitzer, M., Schulten, H.R., 1998. New ideas on the chemical make-up of soil humic and fulvic acids. In: Huang, P.M., (Ed.), Future Prospects for Soil Chemistry, Soil Science Society of America, Madison, pp. 155–178
- Senesi, N., Steelink, C., 1989. Application of ESR spectroscopy to the study of the humic substance. In: Hayes, M.H.B., MacCarthy, P., Malcolm, R.L., Swift, R.S. (Eds.), Humic Substances II. In Search of Structures, Wiley, Chichester, pp. 373–408.
- Sessi, E., Nardi, S., Gessa, C., 2002. Effect of low and high molecular weight humic substances from two different soils on nitrogen assimilation pathway in maize seedlings. Humic Substances in the Environment in press.
- Sladky, Z., 1959. The effect of extracted humus substances on growth of tomato plants. Biologia Plantarum 1, 142–150.
- Stevenson, F.J., 1991. Organic matter—micronutrient reactions in soil. In: Mortvedt, J.J., Cox, F.R., Shuman, L.M., Welch, R.M. (Eds.), Micronutrients in Agriculture, Soil Science Society of America, Madison, pp. 145–186.
- Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reactions, Second ed., Wiley, New York, 496 p.
- Stewart, W.S., Anderson, M.S., 1942. Auxins in some American soils. Botany Gazette 103, 570–575.
- Tan, K.H., 1998. Colloidal chemistry of organic soil constituents. In: Tan, K.H., (Ed.), Principles of Soil Chemistry, Marcel Dekker, New York, pp. 177–258.
- Varanini, Z., Pinton, R., 1995. Humic substances and plant nutrition. In: Lüttge, U., (Ed.), Progress in Botany, vol. 56. Springer, Berlin, pp. 97–117.
- Varanini, Z., Pinton, R., 2001. Direct versus indirect effetcs of soil humic substances on plant growth and nutrition. In: Pinton, R., Varanini, Z., Nannipieri, P. (Eds.), The Rizosphere, Marcel Dekker, Basel, pp. 141–158
- Varanini, Z., Pinton, R., De Biasi, M.G., Astolfi, S., Maggioni, A., 1993. Low molecular weight humic substances stimulated H<sup>+</sup>-ATPase activity of plasma membrane vesicles isolated from oat (*Avena sativa* L.) roots. Plant and Soil 153, 61–69.
- Vaughan, D., 1967a. Effect of humic acid on the development of invertase activity in slices of beetroot tissues washed under aseptic conditions. Humus et Planta IV, 268–271.

- Vaughan, D., 1967b. The stimulation of invertase development in aseptic storage tissue slices by humic acid. Soil Biology & Biochemistry 1, 15–28.
- Vaughan, D., 1986. Effetto delle sostanze umiche sui processi metabolici delle piante. In: Burns, R.G., Dell'Agnola, G., Miele, S., Nardi, S., Savoini, G., Schnitzer, M., Sequi, P., Vaughan, D., Visser, S.A. (Eds.), Sostanze Umiche effetti sul terreno e sulle piante, Ramo Editoriale degli Agricoltori, Roma, pp. 59–81.
- Vaughan, D., MacDonald, I.R., 1971. Effects of humic acid on protein synthesis and ion uptake in beet discs. Journal of Experimental Botany 22, 400–410.
- Vaughan, D., MacDonald, I.R., 1976. Some effects of humic acid on cation uptake by parenchyma tissue. Soil Biology & Biochemistry 8, 415–421.
- Vaughan, D., Ord, B.G., 1981. Uptake and incorporation of <sup>14</sup>C-labelled soil organic matter by roots of *Pisum sativum* L. Journal of Experimental Botany 32, 679–687.
- Vaughan, D., Chesire, M.V., Mundie, C.M., 1974. Uptake by the beetroot tissue and biological activity of <sup>14</sup>C-labelled fractions of soil organic matter. Transactions of the Biochemical Society 2, 126–129.
- Vaughan, D., Malcom, R.E., 1985. Influence of humic substances on growth and physiological processes. In: Vaughan, D., Malcom, R.E. (Eds.), Soil Organic Matter and Biological Activity, Martinus Nijhoff/ Junk W, Dordrecht, The Netherlands, pp. 37–76.
- Vaughan, D., Malcom, R.E., Ord, B.G., 1985. Influence of humic substances on biochemical processes in plants. In: Vaughan, D., Malcom, R.E. (Eds.), Soil Organic Matter and Biological Activit, Martinus Nijhoff/Junk W, Dordrecht, The Netherlands, pp. 77–108.
- Vianello, A., Macrì, F., 1991. Generation of superoxide anion and hydrogen peroxide at the surface of plant cells. Journal of Bioenergetics and Biomembranes 23, 409–423.
- Visser, S.A., 1986. Effetto delle sostanze umiche sulla crescita delle piante. In: Burns, R.G., Dell'Agnola, G., Miele, S., Nardi, S., Savoini, G., Schnitzer, M., Sequi, P., Vaughan, D., Visser, S.A. (Eds.), Sostanze Umiche. Effetti sul Terreno e sulle Piante, Ramo Editoriale degli Agricoltori, Roma, pp. 96–143.
- Visser, S.A., 1987. Effect of humic substances on mitochondrial respiration and oxidative phosphorylation. The Science of the Total Environment 62, 347–354.

National Organic Standards Board Technical Advisory Panel Review compiled by University of California Sustainable Agriculture Research and Education Program (UC SAREP) for the USDA National Organic Program

## **Potassium Silicate**

for use in crop production

## **Executive Summary**

The following petition is under consideration with respect to the USDA NOP Final Rule, Subpart G, the National List of Allowed and Prohibited Substances:

Petitioned:

Addition of potassium silicate to section 205.601(i), "Synthetic substances allowed for use in organic crop production as plant disease control," and to section 205.601(j), "Synthetic substances allowed for use in organic crop production as plant or soil amendments."

The petition requests the use of potassium silicate in organic agriculture for plant disease control and as a plant or soil amendment. The Petition as submitted makes no distinction when petitioning for these two separate uses, and they are henceforth handled jointly in this TAP review.

Potassium silicate is a source of highly soluble potassium and silicon. It is used in agricultural production systems primarily as a silica amendment, and has the added benefit of supplying small amounts of potassium. The NOP has no prior ruling on the use of this substance. The National List allows the use of some synthetic silica-based fertilizers, but they are allowed only as micronutrient amendments as a means to deliver trace metals and are not intended as silica fertilizers per se. The List also allows the use of silicon dioxide in food processing.

Silicon is an essential micronutrient, and deficiencies significantly affect plant health. However, such deficiencies are rare except in cases of silica-accumulating crops (sugarcane, rice) and/or highly weathered soils typical of tropical regions. There are numerous studies on the use of silica amendments to control disease mechanically (when applied as a foliar spray) and physiologically (when used a fertilizer). There is also substantial anecdotal evidence citing the benefits of siliceous substances in organic agriculture. Numerous silica- and non-silica-based alternatives exist, although they may be less effective than potassium silicate. Where needed, the generic mineral glauconite can be used to supply additional silica in significant quantities.

All TAP reviewers agreed that the petitioned substance should be considered synthetic. Two reviewers felt it should be prohibited. One of these reviewers cited the nature of potassium silicate as a highly soluble synthetic fertilizer, and also questioned its effectiveness as a fungicide. The other dissenting reviewer raised similar concerns, questioning the need for silica amendments in organic systems and the legitimacy of supporting evidence. Both of these reviewers indicated that use of the substance in organics should be revisited if and when the need, effectiveness, and mode of action are better demonstrated. The third reviewer was in favor of adding the substance to the List, with annotations. The reviewer viewed the potential benefits as significant, and felt that the substance ultimately is compatible with a system of organic agriculture.

**Summary of TAP Reviewer Analyses** 

Synthetic/ Nonsynthetic	
Synthetic (3)	Reviewer 1: synthetic
Nonsynthetic (0)	Reviewer 2: synthetic
	Reviewer 3: synthetic

Allowed or Prohibited for use as a plant disease control § 205.601(i)	Notes/suggested annotations:		
Allowed (1)	Reviewer 1: Allowed with annotations: not to be derived from industrial byproducts; use limited to		
Prohibited (2)	foliar spray applications to correct silicon deficiencies		
a7 100	Reveiwer 2: Prohibited		
	Reviewer 3: Prohibited		

Allowed or Prohibited for use as a	Notes/suggested annotations:		
plant or soil amendment § 205.601(j)			
Allowed (1)	Reviewer 1: Allowed with annotation: not to be derived from industrial byproducts; use limited to		
Prohibited (2)	foliar spray applications to correct silicon deficiencies		
207	Reveiwer 2: Prohibited		
	Reviewer 3: Prohibited		

This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. This review addresses the requirements of the Organic Foods Production Act to the best of the contractor's ability, and has been reviewed by experts on the TAP. The substance is evaluated against the criteria found in section 2119(m) of the OFPA [7 USC 6517(m)]. The information and evaluation presented to the NOSB is based on the technical evaluation against those criteria, and does not incorporate commercial availability, socio-economic impact or others factors that the NOSB and the USDA may consider in making decisions.

## **Identification**

Chemical name:

potassium silicate

CAS Number: Other Codes: 1312-76-1 None found

Trade name: Other names:

AgSil, KASIL silicic acid potassium salt,

soluble potash glass

## Characterization

#### Composition (variable):

 $K_2Si_2O_5 - K_2Si_2O_2$ 

**Physical Properties:** 

variable

Molecular weight: Appearance:

Fine powder, may be dissolved in aqueous solution.

Color:

Solid is colorless to yellowish; solution

pН

~112

Solubility:

120mg SiO<sub>2</sub> as Si(OH)<sub>4</sub> per liter. Very slowly soluble in cold water, increasingly soluble in water with increasing temperature. Agricultural preparations are soluble in all

proportions. Insoluble in alcohol.

Stability:

Stable under all conditions of use and storage.

Hazardous Polymerization:

Will not occur.

#### Specific Uses

The petition requests the use of potassium silicate in organic agriculture for plant disease control (§205.601(i)) and as a plant or soil amendment (§205.601(j)). The Petition as submitted to the NOP makes no distinction when petitioning for these two separate uses, and they are henceforth handled jointly in this TAP review. Primarily, the beneficial effects of potassium silicate amendments are derived from additions of soluble silica species (predominately SiO<sub>2</sub>) rather than potassium; the intended uses as stated in the petition support the assumption that the substance is used primarily as a silicate fertilizer. Potassium silicate is approved by the USDA as a fertilizer for conventional agriculture, and is used on variety of crops including rice, wheat, barley, sugar cane, melons, grapes, cucurbits, sugar cane, and ornamentals. Potassium silicate is also used to control certain fungal diseases on high value crops.

#### How Made:

Potassium silicates are manufactured using a calcination process that combines silica sand (SiO<sub>2</sub>) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) at 1100-2300°F for up to 15 minutes (NOP Petition; Rawlyk and McDonald 2001). The two substances fuse into glass, which can be dissolved with high-pressure steam to form a clear, slightly viscous fluid, or cooled and ground into a powder. Carbon dioxide is evolved from this reaction. The solution can be dried to form hydrous powder crystals of potassium silicate.

#### **Functionality**

Applications of potassium silicate are primarily intended to provide supplemental silica. Most soils contain significant quantities of silica, but continuous cropping, particularly with crops that accumulate significant quantities of silica, can reduce plant-available levels of Si to the point that supplemental Si fertilization is required. There appears to be a need for Si amendments in temperate as well as tropical crop production systems, and Si fertilizers are applied to crops in several countries for increased productivity and sustainable production (Ma et al. 2001, Korndorfer and Lepsch 2001).

Silicon is the second most abundant element in the earth's crust, and hence is plentiful in most soils. Soluble silica concentrations in soil generally range from 30-40 mg SiO<sub>2</sub> per liter and are dominated by monosilicic acid, Si(OH)<sub>4</sub>. Generally speaking, silicon has not been considered an essential plant nutrient in the past, despite proven beneficial effects of silicon in plant growth and disease prevention (Epstein 1994, 1999, 2000). High silica uptake has been shown to improve drought resistance, increase resistance to fungi and other pathogens, and increase plant growth rate and yield (Marschner 1995, Piorr 1986, Belanger et al. 1995). However, its essentiality as a micronutrient for higher plants is difficult to prove, partly due to the fact that many positive effects of Si are most apparent in cases of abiotic stresses. Silica amendments have also been shown to correct soil toxicities resulting from high levels of soluble Mn<sup>2+</sup>, Fe<sup>2+</sup>, and Al<sup>3+</sup> (Tisdale et al. 1999).

Crop plants differ greatly in their ability to take up silicon. Silica is absorbed by plants as silicic acid, with cereals and grasses containing the highest concentrations (0.2-2.0%). Marschner (1986) divided plants into three major groups, depending on their SiO<sub>2</sub> content: wetland *Gramineae* such as wetland rice, 10-15% (shoot dry weight), dryland *Gramineae*, such as sugar cane and most cereal crops, 1-3%, and legumes and most dicotyledons, <0.5%.

Page 3 of 14

## **Status**

#### OFPA, USDA Final Rule

Potassium silicate is not listed in the Final Rule. Synthetic silicates of zinc, copper, iron, manganese, molybdenum, selenium, and cobalt are allowed as micronutrient plant or soil amendments in cases of documented soil deficiency (§205.601(j)(6)(ii)). In processing applications, silicon dioxide (SiO<sub>2</sub>) is an allowed synthetic.

#### Certification

#### Domestic certifiers

California Certified Organic Farmers (CCOF) Certification Handbook - Not listed (CCOF 2000).

Idaho Department of Agriculture (ISDA) Organic Food Products Rules - Not listed (Section 02.06.33, 2000).

Texas Department of Agriculture (TDA) Organic Certification and Standards Materials List – Not listed. For processing, allows silicon dioxide as a floating agent (2000).

Washington Department of Agriculture (WSDA) Organic Crop Production Standards – Not listed (WAC 16-154-070, 2000). Organic Materials Review Institute (OMRI) Generic Materials List – Not listed (2002).

#### International certifiers

CODEX - Substances Allowed for Use in Soil Fertilizing and Conditioning: - basic slag, in cases of recognized need Substances Allowed for Plant Pest and Disease Control: - mineral powders (stone meal, silicates)

- sodium silicate

- clay silicate (bentonite)

IFOAM - Appendix 1 (Fertilizers and Soil Conditioners) - basic slag of mineral origin

Appendix 2 (Crop Protectants and Growth Regulators) - silicates (e.g. sodium silicate, quartz) of mineral origin.

Canada – Not listed (CGSB 2002). Japan – Not listed (JAS 2001).

#### Regulatory

EPA - Potassium silicate is registered as a pesticide under the Toxic Substance Control Act, and is considered List 3 (Inerts of unknown toxicity) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

FDA - Potassium silicate is considered interchangeable with sodium silicate, a GRAS substance.

IARC - Not listed.

OSHA - Not listed.

NIEHS National Toxicity Program (NTP) - Not listed.

## Section 2119 OFPA U.S.C. 6518(m)(1-7) Criteria

 The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.

Additions of potassium silicate have a very low potential for adverse reactions with other materials used organic farming systems. The substance may react in storage with ammonium salts to form hydrogen gas, and care should be taken to avoid contact with raw manure in closed storage. Potassium silicate solutions have a high pH, and applications may have adverse effects if used on alkali sensitive crops. According to the Petition, mixtures incorporating compost tea or citric acid have been used successfully in the past to lower the pH of potassium silicate solutions.

The toxicity and mode of action of the substance and its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.

Potassium silicate has no known chronic hazards, and neither silica nor potassium appreciably bioconcentrate in the food chain (except with silica in the case of aquatic siliceous species). Potassium silicate contains no volatile organic compounds, and applications will not result in the release of any hazardous or environmentally persistent byproducts (Blumberg 2001).

The breakdown products of the material are potassium and silicon dioxide, both naturally occurring in practically all animal species and ecosystems (King et al. 1938). Diluted potassium silicate solution readily depolymerizes into various silicates are dominated by silicic acid, which is readily absorbed by plants. Dissolved potassium and silica species are indistinguishable from their naturally occurring analogs.

The mode of action of potassium silicate is not fully understood. There appears to be both a mechanical mode of action (when applied as a foliar spray), and a physiological mode of action (when translocated within plant tissues) with current research mostly supporting the latter hypothesis. Silicon impregnates along epidermal cell walls (Parry and Smithson 1964). These layers become effective barriers against water loss and fungal infection (Sangster 1970, Takeoka et al 1984). Silicon

is also deposited in xylem vessel cell walls, preventing constriction of xylem under high transpiration stress (Raven 1983), and in endodermal root cells, where it acts as a barrier against infection of the stele by parasites and pathogens (Bennett 1982). Although there appears to be a relationship between silicate treatments, resistance to fungal attack, and expression of plant defense mechanisms (Cherif et al 1992), a concurrent study (Cherif et al 1992a) showed that accumulation and polymerization of silica at fungal infection sites has no role in providing a physical barrier against fungal attack. Further evidence points to the accumulation of silica in the trichomes of fruit as a possible barrier (Samuels et al 1993).

Potassium silicate has not been tested for ecotoxicity. It is not persistent in aquatic systems, but is highly alkaline in solution form and can be harmful to aquatic life if not diluted and disposed of properly. The following information is based on results from tests using chemically similar sodium silicate on a 100% solids basis (Blumberg 2001):

```
Fish (Gambusia affnis) LD<sub>50</sub> (96h) = 2320ppm

Water fleas (Daphnia magna) LD<sub>50</sub> (96h) = 247 ppm

Snail eggs (Lymnea) LD<sub>50</sub> (96h) = 632 ppm

Amphipoda LD<sub>50</sub> (96h) = 160 ppm
```

#### 3. The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.

As outlined in the "How Made" section, potassium silicate is made via calcination, or thermal conversion into an ashlike powder. The substance is produced by reacting high-silica sand and mined potassium carbonate, yielding potassium silicate and CO<sub>2</sub> gas. The manufacturing process does not appear to pose a substantial risk of environmental contamination, outside of the upstream combustion of fossil fuels to power the reaction. There is no mention in the petition or in other literature of impurities resulting from the reaction, or the use of catalysts other than heat.

While the petitioner intends to use naturally occurring sand as a primary raw ingredient, silica-laden compounds used as silicon fertilizers for conventional agriculture are commonly sourced from industrial byproducts. These byproducts, referred to ubiquitously as slag, are impurities precipitated from the refining of mined materials and smelting of metal ores. Depending on the source, slags may also contain heavy metals associated with their origin or processing (e.g., uranium in phosphate ore, nickel, and zinc). Nonetheless, the use of silica slag fertilizers in agriculture is widespread, particularly in sugarcane fields and paddy rice systems. In conventional agriculture, calcium silicate slag (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> or CaSiO<sub>3</sub>) is commonly used as a silica fertilizer (Tisdale et al 1999). Silicate slag applied at a rate of 1.5-3.0 t/ha is common practice in degraded paddy fields in Japan (Kono 1969, Takahashi and Miyake 1977). Additionally, slag has been used in foreign organic operations in the past. One organic agriculture research farm in Taiwan that used silica slag mixed with manure and soybean meal reported a 25% yield increase of high-quality sponge gourd (Hsieh and Hsieh 1989). If potassium silicate is allowed for organic crop production without specific annotation, it is possible that some silicate fertilizers will be sourced from silica slag.

Solid and aqueous potassium silicate application techniques are unremarkable, and proper use of the material is unlikely to pose a significant risk to the environment. The substance is stable under all conditions of agricultural use and storage (Blumberg 2001). There is no CERCLA Reportable Quantity established for this material, indicating a relatively benign nature. However, as mentioned in Criterion 2, the strongly alkaline solution is potentially toxic to aquatic species. Proper disposal of the bulk material would require neutralization and landfilling or dilution and discharging to sewers in accordance with legal regulations.

#### 4. The effects of the substance on human health.

The effects of potassium silicate applications on human health are likely to be minimal. Potassium is an essential element for humans as a key electrolyte for maintaining basic cardiovascular functions. The use of potassium supplements is commonplace (ANL 2001). An evaluation of the heath aspects of certain silicates as food ingredients determined that potassium silicate is not hazardous when used at levels established for food ingredients (FDA 1978). Sodium silicate, a GRAS substance considered by the FDA to be interchangeable with potassium silicate, has an acute LD<sub>50</sub> (oral, rat) ranging from 1500mg/kg – 3200mg/kg, similar to common table salt (LD<sub>50</sub> = 3000 mg/kg (oral, rat)) (Chao 1978). Potassium silicate is registered for use as a used a corrosion preventative in water at concentrations not greater than 100 ppm (Chao 1978). Silicon dioxide (SiO<sub>2</sub>) is regulated for use as an anticaking agent, and as a stabilizer in beer production [21 CFR 172.480].

When handled and applied in an agricultural setting, the likely routes of entry are absorption through the skin and inhalation. Acute overexposure may cause skin and respiratory tract irritation. The substance has not been tested for primary eye irritation, but is regarded as an eye irritant on the basis of its high alkalinity and its similarity to sodium silicate (Blumberg 2001).

Applications of potassium silicate pose a risk primarily from inhalation or ingestion of silica-rich compounds. Respiratory problems in the agricultural sector due to inhaled dust are a proven concern (Schenker 2000). Decades ago, it was shown that dust arising from storage and handling of wheat grains contained particles that were believed to cause respiratory

ailments (Baker 1961). Burning of high-silica crops, such as rice and sugarcane, have been problematic for worker health in the past (Boeniger et al. 1988). There is also significant indirect evidence linking ingested plant silica and human cancer (Sangster et al. 1983, Bhatt et al. 1984, Hodson et al. 1994), but there currently is no connection between plant silica and inorganic silica sources. Mitigation of health risks associated with respiration of silica-laden dust can be achieved though proper use of personal protective equipment including a NIOSH-approved dust respirator where dust occurs.

No carcinogenicity, mutagenicity, or developmental toxicity data are available for potassium silicate.

#### 5. The effects of the substance on biological and chemical interactions.

The agricultural benefits of silicon amendments on a soil ecosystem are well established. Si has been shown to mitigate adverse effects of climate (Ohyama 1985), water and mineral deficiency (Ma 1988, Ma et al. 2001), salinity (Matoh et al. 1986), and some metal toxicities (Vlamis and Williams 1967, Cocker et al. 1998, Iwasaki and Matsumura 1999).

Silica amendments are proven highly effective at reducing aluminum toxicity (Haak and Siman 1992, Myhr and Erstad 1996) through a variety of mechanisms. Monosilicic acids – the primary soluble form of soil solution silica – can increase soil pH (Lindsay 1979), adsorb to aluminum hydroxides and decrease their mobility (Panov et al. 1982), and form somewhat insoluble substances with Al ions (Lumsdon and Farmer 1995). Soluble silicon compounds can also increase plant tolerance to Al (Rahman et al. 1998). Successive silicate fertilizer applications have been shown to increase soil pH to levels that adversely affect plant growth (Miayke and Takahashi 1983), but soils with high organic matter content tend to buffer this effect, and additions of organic material were effective in correcting soil pH.

Applications of potassium silicate can increase the quantity of mobile phosphates in the soil (Gladkova 1982, Singh and Sarkar 1992, O'Reilly and Sims 1995). In addition to stimulating desorption of phosphate anions from soluble phosphates of calcium, aluminum, iron and magnesium, silica fertilizers also have good adsorption capacity. Application of Si-rich material has the potential to decrease P leaching by 40-70%, while retaining P in a plant-available form (Matichenkov and Bocharnikova 2001).

In addition to altering soil biochemical interactions, numerous studies have demonstrated a connection between potassium silicate fertilization and increased disease and pest resistance. There is significant evidence that silica fertilization may positively affect both silicon-accumulator plants and non-accumulator plants (Korndorfer and Lepsch 2001):

Foliar applications of potassium silicate have been shown to reduce the severity of powdery mildew and increase chlorophyll content and plant growth in strawberries (Wang and Galletta 1998). Potassium silicate did not reduce isolation frequency of *Phytopthora nicotianae* and *Pythium ultimum* or root rot, however it did reduce levels of *T. semipenetrans* (nematode) in soil (Walker and Morey 1999). Potassium silicate has been used in nutrient solutions to control *Pythium* diseases on tomatoes and cucumbers (Adiatia and Besford 1986). An industry-sponsored study showed a foliar potassium silicate spray provided "good to excellent control" of powdery mildew on winegrapes throughout pre-harvest at 630 ppm SiO<sub>2</sub> and 1260 ppm SiO<sub>2</sub> solutions, applied at 500L/ha (McFadden-Smith 2001).

On cucumber plants, silicate fertilizer applied at a rate of 700 or 1400 kg SiO<sub>2</sub>/ha/yr for three years increased plant growth, and reduced damage caused by wilt disease (Miyake and Takahashi 1983). A study demonstrating the uptake of silicate by hydroponic cucumbers showed pronounced resistance to powdery mildew (*Sphaerotheca fuliginea*) when applied at 110 mg/L SiO<sub>2</sub> (Adapt and Bedford 1986). In a greenhouse study, dissolved silicate amendments via drip line reduced damage to cucumbers caused by *Didymelia byronise* (O'Neil 1991).

Crops that accumulate Si such as rice and sugarcane are particularly vulnerable to Si deficiency, and additions of silica fertilizers to soils low in plant-available Si result in marked productivity improvements. Following silicate fertilization in low-Si soil, rice yield increases of ten percent are common and may exceed thirty percent at times of severe leaf blast infection (Yoshida 1981). In one study, applications of sodium silicate (400 kg/ha) on upland rice reduced neck blast (Pyricularia oryzac) and improved overall crop quality (Yamauchi and Winslow 1987). Silica applied to lowland rice soils in Japan since 1955 have resulted in a significant increase in yield (Takahashi et al. 1990). In the US, applications of calcium silicate to rice at up to 6.0 Mg/ha (2.7 t/ac) have been shown to be beneficial (Anderson et al. 1987). Silica slag amendments used on rice systems in Louisiana had a positive effect on the incidence of blast (Pyricularia grisea), sheath blight (Rhizoctonia solani) and brown spot (Bipolaris oryzae) (Bollich et al. 1996). In another study, silicon amendments appear to be effective at very low concentrations; soluble SiO<sub>2</sub> applications of 100 mg/L increased wetland rice yields significantly (Okuda and Takahashi 1965, Takahashi and Miyake 1977).

#### Alternatives to using the substance in terms of practices or other available materials.

#### Soil fertility

Silica is endemic in large quantities in most agroecosystems, and thus there are few organically approved commercial sources of silica fertilizer. Where Si amendments are needed, a number of agricultural products high in silica may be used to supplement soil reserves. These range from field trash, such as rice hulls and sugarcane bagasse, to shells from aquatic

September 4, 2003 Page 5 of 14

animals. Where agricultural solutions are not available or practical, the use of glauconite is a viable alternative. Glauconite is a composite mineral of hydrated iron-potassium silicates (7% K<sub>2</sub>O, 54% SiO<sub>2</sub>). The mineral is mined from naturally occurring sedimentary deposits known as greensand, and has an established history of use as a natural soil conditioner. The substance is commercially available and OMRI-listed.

#### Plant disease control

A number of foliar treatments to control fungal disease are currently used in organic agriculture, with research ongoing; some of these are agricultural products. In one study, an aqueous solution of burnt rice husks (400 q/ha) was shown to be as effective and economically viable as a 1% commercial sodium silicate solution for treatment of rice blast (*Pyricularia oryzae*) (Hsieh and Hsieh 1989). Sulfur is by far the most widespread treatment for powdery mildew and botrytis bunch rot on grapes, and there is a strong agricultural drive for effective organically acceptable controls of fungal disease as copper sulfate falls out of favor due to environmental concerns (Willer et al. 2002, Kauer et al. 2002). Control of grapevine powdery mildew (*Uncinula necator*) in a greenhouse was achieved with applications of *Bacillus subtilis* (94% disease reduction), Synertrol Hort-oil (92%), milk (70%), whey (64%), and Ecocarb (57%) (Crisp et al. 2002). Further reductions were achieved by combining vegetable oils and Ecocarb or whey. Disease suppression by canola oil on grapes (Azam et al. 1998), and by potassium carbonate on sweet peppers (Fallik et al. 1997) and potatoes (Olivier et al. 1998) has also been demonstrated. Another study gave positive results on control of cucurbit powdery mildew with JMS Stylet oil, a biocompatible fungicide (McGrath and Shishkoff 1999). The use of plant extracts such as giant knotweed (Milsana<sup>TM</sup>) and neem tree (Agroneem<sup>TM</sup>, Trilogy<sup>TM</sup>, Triact<sup>TM</sup>) are being investigated for use as fungicides, as well.

#### 7. The compatibility of the substance with a system of sustainable agriculture

From a purely agronomic perspective, potassium silicate appears to be compatible with sustainable agriculture. Si in the soil is continuously removed via crop uptake and by leaching due to desilication processes. There is significant evidence to support the claim that silicon amendments are highly beneficial in some agroecosystems. In addition, the substance contains no persistent or environmentally toxic metabolites, and it appears to pose little risk based on its historical use as a food additive and its chemical similarity to sodium silicate, a GRAS substance.

However, organic law generally does not tolerate the listing of soil amendments that are not naturally occurring in the form that they are used. While the National List allows the use of some synthetic silica-based fertilizers (§205.601(j)(6)(ii)), they are allowed only as micronutrient amendments as a means to deliver trace metals and are not intended as silica fertilizers per se. A strong argument can be made that the substance is ultimately not compatible with organic agriculture based on the fact that it is a fertilizer of high solubility and is not naturally occurring. Furthermore, silica fertilization is largely unnecessary in most soils due to the continuous replenishment by natural soil reserves. Where silica amendments are needed, the availability of a naturally occurring generic substitute (glauconite) makes its inclusion on the National List difficult to justify.

September 4, 2003 Page 6 of 14

<sup>1</sup> Canola-based product

<sup>&</sup>lt;sup>2</sup> Potassium bicarbonate-based surfactant

## Tap Reviewer Discussion

Reviewer 1 [Trained crops agronomist, working as a specialist in organic farmer for a non-profit information provider; 15 years experience in organic education and extension; Central]

Evaluation of the Petition against the Organic Farming Production Act Section 2119 U.S.C. 6518(m)(1-7) Criteria:

1. The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.

There is very little information provided in this section. However, based on an overall reading of the TAP document, I feel satisfied that there is little or no concern that harmful interactions might result. The specific concern cited as regards alkali-sensitive crops strikes me as a hazard due to the improper or ill-advised use of the material; not the sort of hazard that criterion #1 was intended to address.

2. The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.

The only suggestion that there may be an environmental issue with this substance is in the area of disposal. In this instance the concern revolves around the alkaline nature of the substance rather than any innate toxicity. It is hard for me to imagine that farm use is unlikely to result in disposal of enough material to affect an aquatic system—except, perhaps, for a very small pond. In any instance, the use of any amendment in a manner that causes pollution of surface- or ground-waters is a violation of § 205.203 (d), which addresses the mishandling of natural fertilizer materials.

Therefore, I feel that there is no significant cause for concern over the use of potassium silicate, with regard to toxicity or contamination of the environment.

3. The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.

Three issues are highlighted under this criterion: gas emissions, disposal of bulk material, and the possible use of slag.

Fossil fuels are used to drive the chemical reaction that creates potassium silicate, thereby releasing a certain amount of polluting gasses. Also, the chemical reaction, itself, releases CO<sub>2</sub>. However, there is no indication in the information provided that these releases are exorbitant or that they amount to a recognizable hazard.

The disposal of bulk material again appears to be a hazard chiefly from the standpoint of alkalization of the water in aquatic systems. (There is no suggestion of any persistent or insidious pollutants.) I trust that EPA or related regulations are in place to control such "point" pollution.

Much is made in the TAP document of the use of silica-rich slag in international organic production. Slags are prohibited in US organic production, due in large part to the presence of heavy-metal contaminants in many sources. The TAP document suggests that, if approved for organic use, potassium silicate be approved with an annotation that it be manufactured only from naturally occurring sand.

Generally, I believe that that the probability of environmental contamination during manufacture, use, misuse, or disposal, is low and does not present a barrier to use of this substance in organic crop production.

4. The effects of the substance on human health.

The point of concern on this issue revolves around silicate dusts as an inhalation hazard. I concur with the last statement of this section, which suggests that health risks can be adequately mitigated through the proper use of personal protective equipment such as dust respirators. With proper use and common-sense precautions, I feel that potassium silicates do not present a significant human health danger.

5. The effects of the substance on biological and chemical interactions.

I agree that, from an agronomic perspective, the effects are largely, and even highly, positive. Based on evaluation of this criterion, there are good reasons to support use of potassium silicate in organic production.

6. The alternatives to using the substance in terms of practices or other available materials.

Soil fertility: The Functionality section suggests that Si deficiencies may appear under a wide range of US climates and cropping systems. This raises the question of whether the agronomic alternatives cited under #6 are adequate to rectify deficit conditions. The TAP specifically mentions, rice hulls, sugarcane bagasse, and the shells of aquatic animals. I'm

September 4, 2003 Page 7 of 14

under the impression that these by-products are economically available only in certain regions of the country. Much is said about glauconite, which I concur, is a good material. However, it is mined on the East Coast and the cost-plus-shipping is generally considered too high for agronomic use in most areas of the United States. Alternatively, it is reasonable to suppose that other mineral deposits might provide significant amounts of silicon. I checked the label on Azomite®—a rock mineral product that is more available in the West and Midwest; it purports to be 65.85% silica oxide (SiO<sub>2</sub>).

It is important in organic agriculture to remember that the strategy is not to feed the plant directly with readily soluble nutrients, but to enrich the soil and enhance the biological processes that provide crop nutrition in a metered fashion. Theoretically, organic systems utilizing rotations and green manures would replenish the supply of soluble silica from native soil supplies, it being such an abundant element. However, there is no research cited to support or refute this, or to suggest a possible timeframe; we would be taking that on faith as an organic principle.

I am inclined to believe that there are organic alternatives to potassium silicate as a soil amendment/fertilizer, though the material might be allowed for use as a micronutrient to correct deficiencies.

<u>Plant disease control:</u> The TAP document does a good job of listing several of the current fungicidal alternatives. Though there are existing options for pest management, the use of silicates is consistent with organic management. I would be inclined to accept its use as a pest control agent, especially in light of the fact that copper materials are falling into disfavor and sulfur is phototoxic when temperatures increase.

7. Its compatibility with a system of organic agriculture.

The TAP document outlines the compelling arguments under this criterion exceptionally well. Potassium silicate is a benign and generally beneficial material that can easily find a place in organic production systems. However, this argument can be made for a number of synthetic materials such as ammonium sulfate, calcium nitrate, calcium oxide and calcium hydroxide. Organic agriculture does not "short cut" crop nutrition by using soluble fertilizers; the few exceptions involve those materials like sodium nitrate, which are naturally found in a soluble form. And even sodium nitrate has restrictions on its use.

Finally, however, the wording on this criterion is "compatibility with a system of "sustainable" agriculture. I do feel it is compatible with a sustainable agricultural system.

Do you have any additional references?

I have no additional references.

How does the need to apply this substance compare to the ability of organic cropping systems to replenish silica from soil reserves?

I have raised this question above. I will state again that, in theory, a combination of sound cropping practices that includes crop rotations and green manures (that include grasses) should increase the availability of silicon. Where silica has been sorely depleted, I believe there are rock-powder-amendments and organic by-products, which should be available for soil application.

In spite of this, I do believe that potassium silicate should be allowed for use as a micronutrient via foliar fertilization. The contribution to pest resistance is enormous; it is highly consistent with organic principles that maintain nutritional underlies insect pest and disease resistance.

#### Recommendations to the NOSB:

- a) The substance should be considered synthetic on the National List
- a) The substance should be allowed with restrictions for use in organic crop production as a plant disease control and a plant soil amendment.

I believe that potassium silicate should be allowed as a synthetic for pest control under § 205.601 (i) with the annotation that it not be derived from industrial by-products and that it be used only as a foliar spray; it should be allowed as a micronutrient under § 205.601 (j) (6) with the annotation that it not be derived from industrial by-products and that it be used only as a foliar spray to correct or counterbalance silicon deficiencies.

I feel these would be consistent with the decisions made regarding calcium oxide and calcium hydroxide at the May 2002 NOSB meeting in Austin.

\* \* \*

Reviewer 2 [Ph.D. in Crop and Soil Science, specializing in soil fertility and sustainability of managed and natural ecosystems, carbon and nitrogen cycling processes; Pacific]

Evaluation of the Petition against the Organic Farming Production Act Section 2119 U.S.C. 6518(m)(1-7) Criteria:

1. The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.

The substance should have minimal interactions with materials commonly used in organic agriculture when applied to soil or as a foliar application. During storage of the compound, care must be taken to avoid wetting the material. The resulting solution forms a mild alkaline mixture, which may become reactive. When applying it as a solution it may corrode application equipment and harm sensitive plants if not buffered to a neutral pH. Spills are slippery. Reacts with acids, ammonium salts, reactive metals and some organics.

2. The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.

Toxicity of potassium silicate is not well documented but thought to be minimal. When applied as an amendment to soil or foliar application in accordance to application requirements, potassium silicate will have little to no potential to contaminate or persist in the environment. Potassium silicate affects on metabolic interactions are not well characterized if at all. Silicon is inserted mainly in plant cell wall structures. Other metabolic reactions requiring silicon, such as enzymatic, are poorly characterized. Little toxicity information, such as Lethal Dose (LD<sub>50</sub>), is available.

The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.

Solutions can have high pH (alkalinity). Undiluted or un-neutralized solutions are harmful to aquatic life.

The production of potassium silicate is energy intensive requiring temperatures in excess of 1000°F. for synthesis. Potentially large amounts of carbon dioxide can be released during the manufacture of potassium silicate. Additional energy is required to convert solids or liquids into a form suitable for storage and application.

Disposal of potassium silicate will require neutralization.

4. The effects of the substance on human health.

Spray mist or dust may irritate the respiratory tract and cause skin itching and redness. Ingestion of dust or spray causes irritation to esophagus and stomach. Aggravates existing lung and skin medical conditions. Proper guidelines will need to be developed for application if they do not already exist.

5. The effects of the substance on biological and chemical interactions.

Silica is absorbed by plants as silicic acid. Cereals and grasses tend to accumulate the most silicon. Accumulation of silica in these plants can be as high as 20% of the dry weight. Dicotyledons accumulate much less silica. Silica impregnates epidermal and vascular tissue. Reduced lodging, water loss and fungal infections are attributed to adequate silica in these tissues. No biochemical role for silica has been determined.

The application of potassium silicate to soil has been shown to be beneficial. Beneficial effects include reducing the toxic effects of manganese, iron and aluminum. Increased phosphorus availability occurs under beneficial levels of silica. Silica has been shown to be beneficial in impoverished rice soils.

In general, soils contain 20 to 40% silica, which is often adequate for plant demands. Most normal soils have adequate soil solution concentrations of silica in the range of 3 to 40 ppm silica. Rice soils often require in excess of 100 ppm silica. Tropical soils that are highly weathered contain less than 10% silica and may require amendments to correct silica deficiency. Silica deficient soils are often found in high rainfall regions where soils become intensively weathered. These types of soils usually exhibit aluminum toxicity, low base saturation and low pH. Organic management techniques to build soil organic matter often eliminate these poor soil qualities.

6. The alternatives to using the substance in terms of practices or other available materials.

Organic management for soil quality can often eliminate many undesirable soil characteristics that potassium silicate can alleviate. Organic management often results in neutral soil pH reducing toxic effects manganese, iron and aluminum. The increase in soil organic matter results in increased phosphorus availability. The purported beneficial affects of silica on the reduction of disease has only been demonstrated in a few studies. Generally, the conclusion that one can derive from these studies is that silicon has a beneficial effect on reducing some fungal diseases in soils where

September 4, 2003 Page 9 of 14

silicon is low (Schuerger and Hammer 2003; Rodrigues et al 2003; Kim et al. 2002). Many of these studies show beneficial effects in rice and sugarcane but not in other commercial crops. More studies are required to definitively state that silica is useful to prevent fungal infections in other crops. In the United States, low silicon soils are rare. Low silicon soils are general associated with oxisols or highly weathered soils. Highly weathered soils are often found in tropical environments. These soils have lost their primary minerals containing silicon and have weathered to oxides of iron and aluminum. Hawaii may have highly weathered soils and there are reports of beneficial effects of silicon fertilization on sugarcane crops grown on these highly weathered soils. Organic management can often reduce disease through crop diversity and nutrient management. The necessity of potassium silicate for organic production has not been demonstrated.

7. Its compatibility with a system of organic agriculture.

Since potassium silicate has not been demonstrated to be beneficial in organic or conventional cropping systems there is no reason to recommend its use. Certain soils and crops may benefit from silica amendments. Often organic management can alleviate soil problems related to fertility. Addition of composts and green manure are a source of silicon and the addition of organic matter in soil may help to retain silicon. Rice and sugarcane may be obvious exceptions that require silica amendments, especially on impoverished or highly weathered soils.

#### Do you have any additional references?

Rodrigues FA, Vale FXR, Korndorfer GH, Prabhu AS, Datnoff LE, Oliveira AMA, Zambolim L 2003. Influence of silicon on sheath blight of rice in Brazil. CROP PROTECTION 22 (1): 23-29

Kim SG, Kim KW, Park EW, Choi D 2002. Silicon-induced cell wall fortification of rice leaves: A possible cellular mechanism of enhanced host resistance to blast. PHYTOPATHOLOGY 92 (10): 1095-1103

Schuerger AC, Hammer W. 2003. Suppression of powdery mildew on greenhouse-grown cucumber by addition of silicon to hydroponic nutrient solution is inhibited at high temperature. PLANT DISEASE 87 (2): 177-185

The literature on silica is generally small and often conflicting. Generally, only rice and sugarcane crops have shown benefit from silicon additions. Many anecdotal accounts purport the benefits of silica. More research is required to determine the positive biochemical and soil fertility benefits of silica.

# How does the need to apply this substance compare to the ability of organic cropping systems to replenish silica from soil reserves?

Organic systems are designed to recycle nutrients where possible. Addition of nutrients is often achieved through the use of compost. Application of compost derived from lawn clippings and tree pruning would likely add silica to soil. Recycling of crop residues and animal manure will maintain soil silica levels. In general, soil solution silica levels are generally adequate for most crops in organic production.

#### Recommendations to the NOSB:

a) The substance should be considered synthetic on the National List

The substance is manufactured and requires considerable energy during production. The compound is synthesized.

b) The substance should be prohibited for use in organic crop production as a plant disease control and a plant soil

The use of potassium silicate is not required for general organic agricultural done in the United States. Organic management approaches such as cover cropping and use of manure and compost should efficiently recycle silica. Special cases may be considered where high demanding silica crops such as rice and sugarcane are grown on impoverished or highly weathered soils. However, as stated earlier, the use of composts and manure would help to alleviate problems with low silicon in soils. The petition for potassium silicate use in organic agriculture should be revisited if widespread soils of low silicon content for use in organic agriculture can be demonstrated or if scientific studies show in the future the benefits of silicon to soils and disease suppression.

\* \* \*

Reviewer 3

[Ph.D., plant pathology; 13 years organic industry years experience in certification, farm manager, assistant farm advisor, and produce brokerage; agriculture consultant providing on-site technical advice, field monitoring and research for fresh produce growers and shippers; Pacific]

#### Evaluation of the Petition against the Organic Farming Production Act Section 2119 U.S.C. 6518(m)(1-7) Criteria:

The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.
 Potassium silicate has the potential for minor adverse chemical interactions with other materials when used under best management guidelines in agricultural systems. The most important effect would be on alkali sensitive crops due to the high

September 4, 2003 Page 10 of 14

pH of potassium silicate solutions. However, mitigation is easily achieved. If high pH is of concern, the pH can be lowered before or after application by adding acidifying materials from the Allowed Substance List.

Potassium ( $K^+$ ) ion is a natural constituent of soil.  $K^+$  comprises a significant amount of the exchangeable soil solution ions and is an essential macronutrient for plant growth. Soils dominated by kaolinitic clays have more potassium in equilibrium with soil solution that illitic or other 2 to 1 expanding clays. Fertilization of potassium at recommended levels would not be expected to change the behavior of other ions in soil solution substantially. High levels of  $K^+$  may displace  $NH_4^+$  in clays, especially illite and cause leaching of  $NH_4^+$ , but this effect would usually be small under normal fertilization procedures.

Silicon, although very common in soil, is largely unavailable for use by plants, occurring for the most part as an insoluble component of rock and clay. Silicon is an essential micronutrient for some plants such as rice, but much less deficient than potassium: silicon deficient soils are generally highly weathered, tropical soils with high levels of iron oxide and low levels of siliceous minerals. Silicate from potassium silicate at recommended levels would not be expected to change the behaviour of other ions in soil solution detrimentally. Possible benefits include an increase in phosphate desorption from Mg, Ca, Fe and Al to make phosphate available to plants and increased absorption of phosphate to decrease phosphate leaching. Phosphate leaching can be a serious environmental problem. Silicates may reduce the toxicity of high levels of manganese, iron and aluminum.

Potassium silicate has little to none adverse reactions when used under best management guidelines for the application as a fungicide. The high pH of the solution, if uncorrected, would affect tank mixes of materials sensitive to high pH. The reported negative effects potassium silicate has on plant-infecting fungi might also negatively affect naturally or added beneficial fungi in tank mixes or on plant leaves.

- The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.
  - Potassium silicate is nontoxic if used with some precautions. In undiluted form, an alkaline solution it is toxic to aquatic species. Contamination of water must be avoided.
  - The dissolution of potassium silicate in soil solution results in potassium and silicon dioxide ions, which are common in animal species and ecosystems. The potassium ion will react with the cation exchange complex, reaching equilibrium with solution within days of application. Diluting potassium silicate solutions with water results in depolymerization to various silica-based ions, loosely associated with  $K^{+}$ . Foliar sprays are mostly silicic acid and absorbed by plants.
  - The mode of action as a fungicide is unclear. Most importantly, potassium silicate does not seem toxic to fungi, and therefore has fewer dangers to non-target species than toxic materials.
  - Potassium silicate has no chronic hazards, does not bio-concentrate in the food chain, nor makes volatile or toxic organic compounds when used as recommended. Use will not result in hazardous of environmentally persistent byproducts.
- 3. The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance. Large-scale environmental contamination is unlikely from the manufacture, use, misuse or disposal of potassium silicate. Production from high silica sand and mined potassium carbonate produces potassium silicate and CO2, with insignificant direct effects on the environment. However, the significant energy requirement (likely using fossil fuels) for the process can have a range of negative effects. No impurities seem likely.

Use of silica slag instead of sand, which may contain toxic heavy metals, may result in environmental contamination due to errors in properly handling these metals during manufacture and disposal. No information on whether significant amounts of such metals may be present after manufacture of potassium silicate from slags was provided, so I cannot comment on its use.

- 4. The effects of the substance on human health.
  - When used as an agricultural fertilizer or fungicide there should be no adverse effects on human health, provided standard precautions are followed to protect applicators from skin and eye exposure, and inhalation or ingestion. The danger from inorganic silicates is circumstantial, but can be avoided with proper procedures. Crops will not excessively bio-accumulate potassium or silicon and therefore normal consumption of crop or associated products will not introduce toxic levels of potassium in humans. Potassium is an essential element for humans, and silicon dioxide is used in food processing.
- 5. The effects of the substance on biological interactions in the agro ecosystem, including the physiological effects of the substance on soil organisms (including salt index and solubility in the soil (crops, and livestock).
  Potassium silicate when used at recommended application rates will show little to no adverse effects in agro ecosystems. Normal application will not lead to any salinity problems. Adverse pH effects are possible (especially in already alkaline soils), which would alter the makeup of soil organisms, but the pH can be lowered in a variety of ways. Leaching of potassium or ammonium could occur in light textured soils or soils prone to flooding. Normally only minimal leaching loss occurs. Potassium, if applied in excess could interfere with the uptake of other cations especially ammonium. However, these effects should be short-term and not affect yield potential. Soil organisms are not known to be sensitive to potassium and silicon in soil and likely would be only slightly affected. Excess silicate in soil is extremely unlikely, and applications show a neutral or beneficial effect.

September 4, 2003 Page 11 of 14

6. The alternatives to using the substance in terms of practices or other available materials.
No other source of potassium silicate is available, however many sources of potassium and silicate in separate materials are available. Such sources are only valuable as fertilizer, not as fungicides.

Soil Fertility. Alternate sources of potassium range from mined deposits to organic wastes to allowable synthetics. The advantage of pure potassium silicate over mined or organic waste sources is that it reduces the possible excess application of associated nutrients. This could be especially true in the case of organic materials (such as composts and manures) that are managed for their N content. In many cases, excess potassium (excess defined as over recommended application rate) could be applied when managing for specific amounts of N in organic materials. However, the amount of excess potassium in organic materials managed for N would not lead to significant adverse consequences in agro ecosystems. A naturally occurring source of silica (glauconite) has an established history and is available at reasonable cost.

<u>Fungicide</u>. Several foliar fungicides are available. However, all currently listed organically acceptable materials have serious limitations in effectiveness. Two of the most effective allowable synthetics, sulfur and copper, have environmental concerns, and also have limitations. All of the other available materials are frequently ineffective for the diseases that potassium silicate is claimed to control. A different source of potassium silicate (burnt rice husks) has shown similar fungicidal activity as sodium silicate.

7. Its compatibility with a system of organic agriculture.

As a fertilizer, potassium sulfate is not compatible with organic agriculture. As a fungicide, potassium silicate is in-between a prohibited, processed, highly soluble material (generally incompatible with organic agriculture) and an allowed synthetic material that is could be deemed compatible under specific circumstances. Manufacture of potassium silicate from slag could not be successfully evaluated due to lack of information about the process.

#### Concluding remarks

Clearly, potassium silicate is a synthetic because, although the potassium carbonate and sand are mined, they require very high temperature treatment to form potassium silicate, and therefore a significant contribution of fossil fuel or fossil fuel replacement energy.

As a fertilizer, potassium silicate is highly soluble (generally a trait that puts a material in the prohibited grouping) and 'jolts' the soil with a rapid release of nutrients, even though the effects of a rapid availability of potassium and silica is not believed to have nearly as profound an impact as other materials such as sodium nitrate (an allowed non-synthetic material, with restrictions). As a source of potassium or silicate for soil fertility, there are several effective non-synthetic, low soluble alternatives (lack of alternatives can mitigate other prohibited traits). Although synthetic silicates of metallic micronutrients have been allowed, they are not allowed as a source of silica, and probably should remain so: the reason for allowing these synthetic metallic silicates is the lack of acceptable materials, not that they are compatible with organic philosophy. The weight of the above evidence puts potassium silicate as a fertilizer in the prohibited column.

As a fungicide, the same concerns about synthetics are present. However the amounts used are much smaller, there is no 'jolt' to the soil and, most importantly, effective alternatives are not available. Unfortunately, there is not convincing evidence that potassium silicate will be even as effective as the alternatives, and its mode of action is not understood. These are important considerations. Sulfur and copper are allowed synthetics because, although they have some non-target toxicity and environmental troubles, they have a well-understood mode of action and breakdown products, have been used by organic farmers for a long time, and are proven effective. Potassium silicate does not have significant non-target toxicities, environmental risks or breakdown products, but does have a poorly understood mode of action, a short history of use, and has not been proven widely effective.

#### Recommendations to the NOSB:

The substance should be listed as a prohibited synthetic on the National List.

However, I encourage the NOSB to reassess the material, perhaps as a restricted synthetic fungicide if, in the future, the mode of action becomes better understood, and much more significant and widespread effectiveness as a fungicide is proved.

September 4, 2003 Page 12 of 14

#### References

Adapt, MH, Bedford, RT, 1986. Effects of silicon on cucumber plants grown in recirculating nutrient solution. *Annals of Botany* 58(3):343-351.

Adiatia, M, Besford, RT. 1986. Effect of silicon on cucumber plants grown in recirculating nutrient solutions. *Annl. of Bot.* 58:343-351.

Azam, MGN, Gurr, GM, Magarey, PA, 1998. Efficacy of a compound based on canola oil as a fungicide for control of grapevine powdery mildew caused by *Uncinula necator*. Australian Plant Pathology 27(2):116-118.

Baker, G, 1961. Opal phytoliths and adventitious mineral particles in wheat dust, Mineragraphic Investigations Tech. Paper No. 4, C.S.I.R.O., Melbourne, Australia.

Belanger, RR et al, 1995. Soluble Silicon: Its role in crop and disease management of greenhouse crops. *Plant Disease*, Apr 1995, pp329-336.

Bennett, DM. 1982. Silicon deposition in the roots of *Hordeum sativum Jess, Avena sativa L.* and *Triticum aestivum L. Ann Bot* (London) 50:239-245.

Bhatt, T, Coombs, M, O'Neill, CH, 1984. Biogenic silica fiber promotes carcinogenesis in mouse skin. Int. J Cancer 34:519-528.

Bollich, PK, Robichaux, CR, Groth, DE, Oard, JH, Bell, PF. Silicon use in Louisiana rice: potential improvements in disease management and grain yields. *In:* Silicon in Agriculture. Datnoff, LE, Snyder, DH, Korndorfer, GH (eds.). Elsevier Science B.V., 2001. Amsterdam, Netherlands.

Blumberg, JG, 2001. MSDS, AgSil 25H Potassium Silicate. Manufacturer publication, PQ Corporation.

Boeniger, M, Hawkins, M, Marsin, P, Newman, R, 1988. Occupational exposure to silicate fibers and PAHs during sugar cane harvesting. *Ann Occup Hyg* 32:153-169.

Chao, HM. 1978. FDA GRAS Review Branch letter to PQ Corporation. In: Petition to NOSB to allow the use of potassium silicate in organic agriculture.

Cheah, LH, Cox, JK, 1995. Screening of plant extracts for control of powdery mildew in squash. Publication of New Zealand Plant Protection Society.

Cherif, M, Menzies, JG, Benhamou, N, Belanger, RR, 1992. Silicon induced resistance in cucumber plants against *Pythium ultimum*. *Physiological and Molecular Plant Pathology* 41(6):411-425.

Cherif, M, Menzies, JG, Benhamou, N, Belanger, RR, 1992a. Studies of silicon distribution in wounded and *Pythium ultimum infected* cucumber plants. *Physiological and Molecular Plant Pathology* 41(5):371-385.

Cocker, KM, Evans, DE, Hodson, MJ. 1998. Amelioration of aluminum toxicity by silicon in higher plants: sloution chemistry or an *in planta* mechanism? *Physiol. Plant.* 104:608-614.

Crisp, P, Scott, E, Wicks, T. Novel control of grapevine powdery mildew. IFOAM Proceedings, 7<sup>th</sup> Int'l Congress on Organic Viticulture and Wine. August 20-21, 2002, Victoria, British Columbia, Canada.

Epstein, E. 1994. The anomaly of silicon in agriculture. Proc. Natl. Acad. Sci. USA 91:11-17.

Epstein, E. 1999. Silicon. Annu. Rev. Plant Physiol. Plant Molec. Biol. 50:641-664.

Epstein, E. 2000. The discovery of the essential elements. In: Discoveries in Plant Biology, v3, Kung, S-D and Yang, S-F, eds. World Scientific Publishing, Singapore, in press.

Fallik, E, Ziv, O, Grinberg, S, Alkalai, S, Klein, JD, 1997. Bicarbonate solutions control powdery midew (*Leveillula taurica*) on sweet red pepper and reduce the development of postharvest fruit rotting. Phytoparasitica 25(1):41-43.

Gladkova, KF. 1982. The role of silicon in phosphate plant nutrition. Agrochemistry 2:133.

Haak, E, Siman, G, 1992. Field experiments with Oyeslag (Faltlorsok med Oyeslag). Report 185, Uppsala.

Herger, G, Klingauf, F, Mangold, D, Pommer, EH, Scherer, M, 1988. Effect of extracts of Reynoutria sachalinensis (F. Smith) Nakai (Polygonaceae) against fungal diseases, especially powdery mildews. (In German), Nachrichtenbl. Deut. Pfanzenschulzd (Braunschweig) 40:56-60.

Hodson, MJ, Smith, RJ, Van Blaaderen, A, Crafton, T, and O'Neill, CH, 1994. Detecting plant silica fibers in animal tissue by confocal florescence microscopy. *Ann Occup. Hyg.* 38:149-160.

Hsieh, S.C. and C.F. Hsieh. 1989. Organic Farming. Special Pub. No. 16 of Taichung District Agricultural. Improvement Station, Taiwan. 307pp. (In Chinese).

Iwasaki, K, Matsumura, A. 1999. Effect of silicon on alleviation of manganese toxicity in pumpkin (Cucurbita moschata Duch cv. Shintosa). Soil Sci Plant Nutr. in press.

Kauer, R, Berkelmann, B, Uhl, J, Schmidt, M. Downy and powdery mildew in organic viticulture: safer control with less copper and sulphur. IFOAM Proceedings, 7<sup>th</sup> Int'l Congress on Organic Viticulture and Wine. August 20-21, 2002, Victoria, British Columbia, Canada.

King, EJ, Belt, TH. 1938. Physiological and pathological aspects of silica. Physiol. Rev. 18:329-365.

Korndorfer, GH, Lepsch, I. 2001. Effect of silicon on plant growth and crop yield. In: Silicon in Agriculture. Datnoff, LE, Snyder, DH, Korndorfer, GH (eds.). Elsevier Science B.V., Amsterdam, Netherlands.

Lindsay, WL, 1979. Chemical Equilibria in Soil. John Wiley & Sons, New York.

Lumsdon, DG, Farmer, VC, 1995. Solubility characteristics of proto-imogolite soils: how silicic acid can detoxify aluminum solutions. *European Soil Sci.* 46:179.

Ma, JF. 1988. Study on physiological role of silicon in rice plants. Master thesis, Kyoto University.

Ma, JF, Miyake, Y, Takahashi, E. 2001. Silicon as a beneficial element for crop plants. *In:* Silicon in Agriculture. Datnoff, LE, Snyder, DH, Korndorfer, GH (eds.). Elsevier Science B.V., Amsterdam, Netherlands.

Marschner, H, 1986. Mineral nutrition of higher plants. Academic Press, London, England.

September 4, 2003 Page 13 of 14

- Matichenkov, VV, Bocharnikova, EA. The relationship between silicon and soil physical and chemical properties. *In:* Silicon in Agriculture. Datnoff, LE, Snyder, DH, Korndorfer, GH (eds.). Elsevier Science B.V., 2001. Amsterdam, Netherlands.
- Matoh, T, Kairusmee, P, Takahashi, E. 1986. Salt-induced damage to rice plants and alleviation effect of silicate. Soil Sci. Plant Nutr. 32:295-304.
- McFadden-Smith, W, 2001. Control of powdery mildew with potassium silicate. Unpublished industry trial, in cooperation with Vineland Agricultural Research Station, Ontario, Canada.
- McGrath, MT, Shiskkoff, N, 1999. Evaluation of biocompatible products for managing cucurbit powdery mildew. *Crop Protection* 18(7):471-478.
- Miyake, Y, Takahashi, E, 1983. Effects of silicon on the growth of cucumber plant in soil culture. Soil Science and Plant Nutrition 29(4):463-471.
- Myhr, K, Erstad. K, 1996. Converter slag as a liming material on organic soils. Norwegian J. Agric. Sci. 10:81.
- Ohyama, N. 1985. Amelioration of cold weather damage of rice by silicate fertilizer application. Agric. Hort. 60:1385-1389.
- Okuda, A, and Takahashi, E. 1965. The role of silicon. Mineral Nutrition Rice Plant, Proc. Symp. IRRI 1964, pp123-146.
- Olivier, C, Halseth, DE, Mizubuti, ESG, Loria, R, 1998. Postharvest application of organic and inorganic salts for suppression on potato tubers. Plant Disease 82(2):213-217.
- O'Neil, TM. Investigation of glasshouse structure, growing medium and silicon nutrition as factors affecting disease incidence in cucumber crops. *Medelingen van de Faculteit Landbouwwetenschappen, Rijksuniversiteit Gent* 56(2b):359-367. Presented at 43<sup>rd</sup> Int'l Symposium on Crop Protection, Ghent, Belgium. 7 May 1991.
- O'Reilly, SE, Sims, JT, 1995. Phosphorous adsorption and desorption in a sandy soil amended with high rates of coal fly ash. Com Soil Sci. and Plant Anal. 26:2983.
- Panov, NP, Goncharova, NA, Rodionova, LP, 1982. The role of amorphous silicic acid in solonetz soil processes. Vestnik Agr. Sci. 11:18.
- Parry, DW, Smithson, F. 1964. Types of opaline silica deposition in the leaves of British grasses. *Ann. Bot. (London)* 28:169-185. Piorr, HP, 1986. Reducing Fungicide Applications by Using Sodium Silicate and Wettable Sulphur in Cereals. Med. Fac. Landbouww. Rijksuniv. Gent, 51/2b.
- Rahman, MT, Kawamura, K, Koyama, H, Hara, T, 1988. Varietal differences in the growth of rice plants in response to aluminum and silicon. Soil Sci. Plant Nutr. 44:423.
- Raven, JA. 1983. The transport and function of silicon in plants. Biol. Review Cambridge Philos. Soc. 58(2):179-207.
- Rawlyk D, McDonald M. Potassium silicate-based drilling fluids: an environmentally friendly drilling fluid providing higher rates of penetration. CADE/CAODC Drilling Conference, October 23-24 2001. Calgary, Alberta Canada.
- Samuels, AL, Glass, ADM, Ehret, DL, Menzies, JG. 1993. Effects of silicon supplementation on cucumber fruit: changes in surface characteristics. *Annals of Botany* 72(5):433-440.
- Sangster AG. 1970. Intracellular silica deposition in immature leaves in three species of the *Gramineae*. Ann. Bot. (London) 34:245-257.
- Sangster AG, Hodson MJ, Parry, DW, 1983. Silicon deposition and anatomical studies in the inflorescence bracts of four Phalaris species with their possible relevance to carcinogenesis. *New Phytol.* 93:105-122.
- Shenker, M, 2000. Exposure and health effects from inorganic agricultural dusts. Environmental Health Perspectives 108:661-664
- Singh, KP, Sarkar, MC. 1992. Phosphorous availability in soil as affected by fertilizer phosphorous, sodium silicate and farmyard manure. *J. Indian Soc. Soil Sci.* 40:762.
- Takahashi, E, Miyake, Y, 1977. Silica and plant growth. Proc. Int. Semin. Soil Environ. Fert. Manage. Intensive Agric., pp603-611.
- Takahashi, E, Ma, JF, and Miyake, Y. 1990. The possibility of silicon as an essential element for higher plants. Comments Agric. Food Chem. 2:99-122.
- Takeoka, Y, Wada, T, Naito, K, Kaufman, PB. 1984. Studies on silification of epidermal tissues of grasses as investigated by soft X-ray image analysis. II. Differences in frequency of silica bodies in bulliform cells at different positions in the leaves of rice plants. *Japanese J Crop Sci* 53:197-203.
- Tisdale, SL, Havlin, JL, Beaton, JD, Nelson, WL. 1999. Soil Fertility and Fertilizers, An Introduction to Nutrient Management, 6th Ed. Prentice-Hall, Upper Saddle River, NJ.
- Walker, GE, Morey , BG. 1999. Effects of Chemical and Microbial Antagonists on Nematode and Fungal Pathogens of Citrus Roots. Australian J Exper. Agri. 39:629-637.
- Wand, SY, Galletta, GJ, 1998. Foliar application of potassium silicate induces metabolic changes in strawberry plants. *J Plant Nutr.* 21(1):157-167.
- Vlamis, J, Williams, DE. 1967. Manganese and silicon interaction in the Gramineae. Plant Soil 20:221-231.
- Willer, H, Haeseli, A, Levite, D, Tamm, L. Organic Viticulture in Europe. IFOAM Proceedings, 7<sup>th</sup> Int'l Congress on Organic Viticulture and Wine. August 20-21, 2002, Victoria, British Columbia, Canada.
- Yoshida, S. 1981. Fundamentals of rice crop science. International Rice Research Institute, Los Banos, Laguna, Philippines.

September 4, 2003 Page 14 of 14

## Update on Signaling

# Salicylate, A New Plant Hormone<sup>1</sup>

#### Ilya Raskin

AgBiotech Center, Rutgers University, Cook College, P.O. Box 231, New Brunswick, New Jersey 08903-0231

Centuries ago, the American Indians and ancient Greeks independently discovered that the leaves and bark of the willow tree cured aches and fevers. It was not until 1828 that Johann Buchner, working in Munich, successfully isolated a tiny amount of salicin, the glucoside of salicyl alcohol, which was the major salicylate in willow bark (for review see ref. 23). The name SA<sup>2</sup>, from the Latin word Salix for willow tree, was given to this active ingredient of willow bark by Raffaele Piria in 1838. The first commercial production of synthetic SA began in Germany in 1874. Aspirin, a trade name for acetylsalicylic acid, was introduced by the Bayer Company in 1898 and rapidly became one of world's best-selling drugs. In spite of the fact that the mode of medicinal action of salicylates is a subject of continual debate, they are being used to treat human diseases ranging from the common cold to heart attacks. Because even in aqueous solutions aspirin undergoes spontaneous hydrolysis to SA, the two compounds have similar effects in plants and will be treated together in this review.

Salicylic or *ortho*-hydroxybenzoic acid belongs to a diverse group of plant phenolics. These are compounds with an aromatic ring bearing a hydroxyl group or its functional derivative. The most important mechanism for formation of benzoic acids in plants is the side chain degradation of cinnamic acids, which are important intermediates in the shikimic acid pathway (Fig. 1B). The conversion of cinnamic acid to SA is likely to proceed via benzoic or *ortho*-coumaric acid (1). A recent survey of SA content in the leaves and reproductive structures of 34 plant species confirmed its ubiquitous distribution in plants (14). The highest levels of SA were found in the inflorescences of thermogenic plants and in plants infected with necrotizing pathogens (see below).

#### SA AND FLOWERING

The first indication of the flower-inducing effects of SA was obtained in an organogenic tobacco tissue culture supplemented with kinetin and IAA (9), but these observations never attracted much attention because a number of different molecules were found to be active in inducing flower bud

formation in tobacco cell cultures (4). The first suggestion that SA may be involved in the regulation of flowering came from experiments in which aphids were allowed to feed on vegetative and reproductive forms of the short-day plant Xanthium strumarum. It was hypothesized that a phloemtransmissible factor responsible for the induction of flowering could be found in the honeydew excreted by aphids. Different fractions of honeydew were tested in a bioassay system using Lemna gibba strain G3, a long-day plant, kept in a noninductive light cycle. The flower-inducing substance from X. strumarum was identified as SA, which at 5.6 μM caused a maximal induction of L. gibba flowering (2). The stimulatory effect of SA on flowering was later demonstrated in other species of Lemnaceae, both short- and long-day, in Oncidium, an ornamental orchid species, in Impatiens balsamina, a qualitatively short-day plant, in Arabidopsis thaliana, and in Pisita stratiotes L. (Araceae).

The possibility that SA functions as the endogenous regulator of flowering in *Xanthium*, Lemnaceae, or other plants was diminished by the fact that SA did not induce flowering in *X. strumarum* and that the levels of SA were not different in honeydew collected from vegetative and flowering plants. Also, no changes in the endogenous levels of SA in vegetative or flowering *Lemna* have been reported. In addition, the SA effect was not specific: a large variety of benzoic acids (22), nonphenolic compounds (including chelating agents), ferricyanide, nicotinic acid, and cytokinins induced flowering in *Lemna* maintained under a noninductive photoperiod. In a number of species, SA promoted flowering in combination with other regulatory molecules (e.g. gibberellins).

# THERMOGENIC PLANTS AND SEARCH FOR CALORIGEN

Thermogenicity (heat production) in plants, first described by Lamarck in 1778 (8) for the genus *Arum*, is now known to occur in the male reproductive structures of cycads and in the flowers or inflorescences of some angiosperm species belonging to the families Annonaceae, Araceae, Aristolochiaceae, Cyclanthaceae, Nymphaeaceae, and Palmae (11). The heating is believed to be associated with a large increase in the cyanide-insensitive nonphosphorylating electron transport pathway unique to plant mitochondria (7). The increase in the use of this alternative respiratory pathway is so dramatic that oxygen consumption in the inflorescences of *Arum* lilies at the peak of heat production is as high as that of a hummingbird in flight. In addition to activation of the alternative oxidase, thermogenicity involves activation of glyco-

<sup>&</sup>lt;sup>1</sup> Support from the New Jersey Commission for Science and Technology, the U.S. Department of Agriculture/Competitive Research Grants Office, and the Division of Energy Biosciences of the U.S. Department of Energy

<sup>&</sup>lt;sup>2</sup> Abbreviations: SA, salicylic acid; HR, hypersensitive reaction; SAR, systemic acquired resistance; PR, pathogenesis-related; TMV, tobacco mosaic virus.

lytic and Krebs cycle enzymes, which provide substrates for this remarkable metabolic explosion.

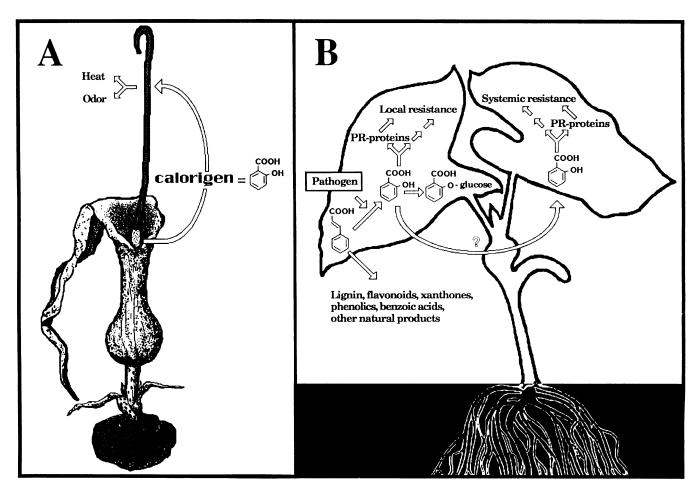
In one of the *Arum* lilies, *Sauromatum guttatum* Schott (voodoo lily), the temperature of the upper part of the spadix known as the appendix increases by 14°C above the ambient temperature on the day of blooming (Fig. 1A). The heat facilitates the volatilization of foul-smelling amines and indoles that are attractive to insect pollinators. In 1937, Van Herk (20) suggested that the burst of metabolic activity in the appendix of the voodoo lily is triggered by "calorigen," a water-soluble substance produced in the male (staminate) flower primordia located just below the appendix.

Van Herk's ideas encountered some skepticism, partially because attempts to isolate and characterize calorigen were not successful until recently. However, in 1987 an attempt to identify the elusive calorigen ended in success. Mass spectroscopic analysis of highly purified calorigen extracted from the male flowers of voodoo lily indicated the presence of SA

(13). Application of SA at  $0.13~\mu g~g^{-1}$  fresh weight to sections of the immature appendix led to temperature increases of as much as 12°C. These increases duplicated the temperature increases produced by the crude calorigen extract both in magnitude and timing, indicating that SA is calorigen. The sensitivity of the appendix tissue to SA increased daily with the approach of anthesis and was controlled by the photoperiod.

On the day preceding the day of blooming, the levels of SA in the appendix of the voodoo lily increased almost 100-fold to 1  $\mu$ g g<sup>-1</sup> fresh weight (15). The concentration of SA in the appendix tissue returned to basal, preblooming levels at the end of the thermogenic period. Of 33 analogs of SA tested, only 2,6-dihydroxybenzoic acid and aspirin were thermogenic and induced odor production (15).

The nuclear gene from *S. guttatum* encoding the alternative oxidase protein with an estimated molecular mass of 38.9 kD was recently isolated and characterized (17). Both calorigen



**Figure 1.** Proposed action of salicylic acid in thermogenesis (A) and disease resistance (B). A, On the day before blooming, calorigen, identified as SA, moves from the male flowers of voodoo lily to the appendix. There it induces heat and the production of odor attractive to insect pollinators. The heat is a product of cyanide-insensitive respiration, which, along with the enzymes of the Krebs cycle and glycolysis, is induced by SA. The mechanism by which SA induces thermogenesis still remains a mystery. B, During the development of the hypersensitive response to pathogens, large amounts of SA are produced from cinnamic acid in the vicinity of necrotic lesions. A large portion of the SA is immobilized as  $\beta$ -O-p-glucosylsalicylic acid. Free SA enters the phloem and can be detected in upper leaves. Increases in SA are sufficient for the systemic induction of PR proteins and resistance to subsequent infection. It is still unclear whether or not the export of SA from the infected leaf can account for all of the SA present in the plant during SAR.

extract and SA cause the induction of the alternative oxidase gene, providing additional confirmation of the chemical identity of calorigen. Although the mechanism involved in SA induction of alternative respiration is being unraveled, the mechanism by which SA stimulates glycolysis, the Krebs cycle, and odor production during thermogenesis still remains a mystery.

The discovery of the role of SA in the flowering of thermogenic plants was the first demonstration of an important regulatory role played by endogenous SA. The study ended a 50-year-long search for calorigen and laid the foundation for ongoing investigations of other processes that may be regulated by SA in plants. This discovery also moved SA research from the stage of collecting phenomenological observations to that of making serious attempts to understand the mechanisms of SA action. It is important to remember that both heat and scent production are an integral part of flowering in thermogenic plants. Considering the numerous reports on the induction of flowering by SA (see above), it is tempting to speculate that endogenous SA may play a role in the regulation of certain events in flowering of plants that are not overtly thermogenic.

#### SA AND DISEASE RESISTANCE IN PLANTS

Some disease-resistant plants restrict the spread of fungal, bacterial, or viral pathogens to a small area around the point of initial penetration, where a necrotic lesion appears. This protective cell suicide is referred to as the HR. The HR may lead to SAR, which is defined as a resistance to subsequent pathogen attack that develops in the uninfected, pathogen-free parts of the plant after the initial inoculation (18). SAR develops in a variety of plant interactions with lesion-forming pathogens, is detected several days after the initial infection, can last for several weeks, and is effective against a broad range of pathogens that may be unrelated to the inducing organism.

Commonly associated with HR and SAR is the systemic synthesis of several families of serologically distinct, low mol wt, PR proteins. The localization, timing of appearance, and defense-related functions of at least some PR proteins suggest their possible involvement in SAR. However, definitive proof that the induction of PR proteins causes SAR is still lacking.

It is well established that resistance to pathogens and the production of some PR proteins in plants can be induced by SA or acetylsalicylic acid, even in the absence of pathogenic organisms. The discovery of a protective function of salicylates was made in 1979 in tobacco (*Nicotiana tabacum* cv Xanthi-nc) (24). Xanthi-nc tobacco contains the "N" gene, which originates from N. glutinosa and confers HR response to TMV. Salicylate treatments also resulted in the induction of PR-1 proteins in treated leaves. The level of PR protein induction and TMV protection increased with increasing aspirin concentrations. A recent comprehensive study utilizing modern molecular approaches showed that nine classes of PR protein mRNAs that are induced during the development of SAR to TMV in tobacco can be induced by SA to a similar degree (21).

In TMV-susceptible *N. tabacum* containing the recessive "n" allele, TMV does not trigger the induction of PR proteins

and HR. Instead, the virus spreads systemically, causing a characteristic mosaic in younger leaves. However, aspirin induces PR proteins in "n" tobacco and simultaneously reduces the spread and total accumulation of TMV (25). The extent to which SA-induced resistance is based on the induction of PR proteins is still unknown. It is certainly possible that SA activates other resistance mechanisms.

Because SAR can be induced systemically by localized infections, the existence of a systemic signal that activates PR proteins and/or other resistance mechanisms has been hypothesized for at least 25 years (19). Evidence from stem girdling and grafting experiments suggests that the putative signal moves through the phloem tissue of the vascular system of the plant. (6).

The observations that exogenous SA applications induce resistance and PR proteins in plants and that SA is an important endogenous messenger in thermogenic plants, together with the development of analytical methods to quantify its endogenous levels in plant tissues (15), prepared the way to test the possibility that SA is an endogenous messenger that activates important elements of host resistance to pathogens. The single-gene inheritance of TMV resistance in tobacco provided a suitable experimental system in which to investigate this possibility.

A new chapter in SA research started from the observation that SA levels in TMV-resistant (Xanthi-nc), but not susceptible (Xanthi), tobacco increase almost 50-fold, to 1  $\mu$ g g<sup>-1</sup> fresh weight, in TMV-inoculated leaves and 10-fold in uninfected leaves of the same plant (10) (Fig. 1B). Induction of PR-1 genes paralleled the rise in SA levels. Although TMV induced PR proteins only in Xanthi-nc tobacco, SA was effective in both Xanthi "n" and Xanthi-nc "N" plants. By feeding SA to excised leaves of Xanthi-nc "NN" tobacco, it was shown that the observed increase in endogenous SA levels is sufficient for the systemic induction of PR-1 proteins (26) and increased resistance to TMV (5). TMV infection becomes systemic and Xanthi-nc plants fail to accumulate PR-1 proteins at 32°C. This loss of HR at high temperature was associated with an inability to accumulate SA. However, spraying leaves with SA induced PR-1 proteins at both 24 and 32°C (26).

SA is also exported from the primary site of infection to the uninfected tissues (26). When leaves of Xanthi-nc tobacco were excised 24 h after TMV inoculation and exudates from the cut petioles were collected, the increase in endogenous SA in TMV-inoculated leaves paralleled SA levels in exudates. Exudation and leaf accumulation of SA were proportional to TMV concentration. Different components of TMV were compared for their ability to induce SA accumulation and exudation: three different aggregate states of coat protein failed to induce SA, but unencapsidated viral RNA elicited SA accumulation in leaves and phloem (26). Mechanical leaf injury did not stimulate SA production and exudation.

The highest concentrations of free SA are observed in and around hypersensitive lesions (5). Chemical and enzymic hydrolysis of extracts from TMV-inoculated leaves demonstrated the presence of an SA conjugate tentatively identified as  $\beta$ -O-D-glucosylsalicylic acid (5) (Fig. 1B). The SA-glucoside was immobile and could be detected only in tissue that contained necrotic lesions. It was not detected in phloem

exudates or virus-free leaves of TMV-inoculated Xanthi-nc tobacco

Another set of experiments has demonstrated that a fluorescent metabolite identified as SA increased dramatically in the phloem of cucumber plants inoculated with tobacco necrosis virus or the fungal pathogen Colletotrichum lagenarium (12). Levels of SA increased transiently after inoculation and reached a peak before SAR was detected. However, analysis of phloem exudate from cucumber leaves demonstrated that the earliest detectable increase in SA occurred 8 h after inoculation with Pseudomonas syringae pv syringae (16). The systemic accumulation of SA was observed even when the inoculated leaf remained attached to the plant for only 4 h. Although supporting the role of SA as a component of the transduction pathway leading to resistance, these results suggest that another chemical signal may be required for the systemic accumulation of SA in cucumber.

At present, the experimental evidence supports the hypothesis that SA acts as an endogenous signal in induction of PR proteins and at least some components of SAR (Fig. 1B). This conclusion is based on the fact that SA meets the essential criteria of a signal molecule, namely: (a) SA induces resistance to pathogens; (b) SA induces PR proteins; (c) SA levels increase locally and systemically following pathogen attack; and (d) SA moves throughout the plant via phloem.

#### **CONCLUDING REMARKS**

Centuries have passed since the healing substance from willow bark was shown to have value not only for humans but for the plants that synthesize it. Surprisingly, some of the effects of SA in plants are also associated with reduction of disease symptoms. We still do not know if there are any connections between the therapeutic effects of salicylates in plants and animals.

Although all indications are that SA regulates some aspects of disease resistance and thermogenesis, we still do not understand the biochemical link between the action of SA in plant disease resistance and its thermogenic and odor-producing effects in *Arum* lilies. It is also important to elucidate the pathway(s) of SA biosynthesis and metabolism and identify genes involved in these pathways. Furthermore, the molecular components of the SA signal transduction pathway(s) should be elucidated and other possible regulatory functions for SA in plants investigated.

The growing appreciation of the role of SA in plants may bring some practical applications. For example, manipulating the level of SA in plants may be a promising area for the application of biotechnology to crop protection. Increases in endogenous SA may be achieved via enhancing transcription and translation of the genes for SA biosynthesis or by blocking the expression of genes involved in SA metabolism. Engineering transgenic plants with elevated SA levels may be the first step in the creation of crops with increased resistance to agronomically important pathogens.

The classic definition of a plant hormone suggests that it is an organic substance that acts in small quantities at some distance from the site of its synthesis. This definition virtually equates plant and animal hormones. A more recent and probably more universal definition simply states that a plant

hormone is a "natural compound in plants with an ability to affect physiological processes at concentrations far below those where either nutrients or vitamins would affect these processes" (3). All the information on the role of SA in thermogenesis and disease resistance suggests that SA meets these qualifying criteria for a plant hormone.

#### LITERATURE CITED

- Chadha KC, Brown SA (1974) Biosynthesis of phenolic acids in tomato plants infected with Agrobacterium tumefaciens. Can J Bot 52: 2041–2046
- Cleland FC, Ajami A (1974) Identification of the flower-inducing factor isolated from aphid honeydew as being salicylic acid. Plant Physiol 54: 904-906
- Davies PJ (1988) The plant hormones: their nature, occurrence, and functions. In PJ Davies ed, Plant Hormones and Their Role in Plant Growth and Development. Academic Publishers, Dordrecht, pp 1–11
- Eberhard S, Doubrava N, Marta V, Mohnen D, Southwick A, Darvill A, Albersheim P (1989) Pectic cell wall fragments regulate tobacco thin-cell-layer explant morphogenesis. Plant Cell 1: 747–755
- Enyedi AJ, Yalpani N, Silverman P, Raskin I (1992) Localization, conjugation, and function of salicylic acid in tobacco during hypersensitive reaction to tobacco mosaic virus. Proc Natl Acad Sci USA 89: 2480–2484
- Guedes MEM, Richmond S, Kuc J (1980) Induced systemic resistance to anthracnose in cucumber as influenced by the location of the inducer inoculation with Colletotrichum lagenarium and the onset of flowering and fruiting. Physiol Plant Pathol 17: 229-233
- James WO, Beevers H (1950) The respiration of Arum spadix. A rapid respiration, resistant to cyanide. New Phytol 49: 353-374
- 8. Lamarck JB (1778) Flore Francaise 3. L'Imprimerie Royale, Paris, pp 537–539
- Lee TT, Skoog F (1965) Effect of substituted phenols on bud formation and growth of tobacco tissue culture. Physiol Plant 18: 386–402
- Malamy J, Carr JP, Klessig DF, Raskin I (1990) Salicylic acid: a likely endogenous signal in the resistance response of tobacco to viral infection. Science 250: 1002–1004
- 11. **Meeuse BJD, Raskin I** (1988) Sexual reproduction in the arum, lily family, with emphasis on thermogenicity. Sex Plant Reprod 1: 3–15
- Metraux JP, Signer H, Ryals J, Ward E, Wyss-Benz M, Gaudin J, Raschdorf K, Schmid E, Blum W, Inverardi B (1990) Increase in salicylic acid at the onset of systemic acquired resistance in cucumber. Science 250: 1004–1006
- Raskin I, Ehmann A, Melander WR, Meeuse BJD (1987)
   Salicylic acid—a natural inducer of heat production in Arum lilies. Science 237: 1545–1556
- Raskin I, Skubatz H, Tang W, Meeuse BJD (1990) Salicylic acid levels in thermogenic and non-thermogenic plants. Ann Bot 66: 376–373
- Raskin I, Turner IM, Melander WR (1989) Regulation of heat production in the inflorescences of an Arum lily by endogenous salicylic acid. Proc Natl Acad Sci USA 86: 2214–2218
- Rasmussen JB, Hammerschmidt R, Zook MN (1991) Systemic induction of salicylic acid accumulation in cucumber after inoculation with Pseudomonas syringae pv syringae. Plant Physiol 97: 1342–1347
- Rhoads DM, McIntosh L (1991) Isolation and characterization of a cDNA clone encoding an alternative oxidase protein of Sauromatum guttatum (Schott). Proc Natl Acad Sci USA 88: 2122-2126
- Ross AF (1961) Systemic acquired resistance induced by localized virus infections in plants. Virology 13: 340–358
- 19. Ross AF (1966) Systemic effects of local lesion formation. In

- ABR Beemst, J Bijkstra, eds, Viruses of Plants. North Holland, Amsterdam, pp 127-150
- Van Herk AWH (1937) Die chemischen Vorgänge im Sauromatum-Kolben. III. Mitteilung. Proc K Ned Akad Wet 40: 709-719
- 21. Ward ER, Uknes SJ, Williams SC, Dincher SS, Wiederhold DL, Alexander DC, Ahl-Goy P, Metraux J-P, Ryals JA (1991) Coordinate gene activity in response to agents that induce systemic acquired resistance. Plant Cell 3: 1085-1094
- Watanabe K, Fujita T, Takimoto A (1981) Relationship between structure and flower-inducing activity of benzoic acid derivatives in *Lemna paucicostata* 151. Plant Cell Physiol 20: 847-850
- 23. Weissmann G (1991) Aspirin. Sci Am 264: 84-90
- White RF (1979) Acetylsalicylic acid (aspirin) induces resistance to tobacco mosaic virus in tobacco. Virology 99: 410–412
- 25. **White RF, Antoniw JF, Carr JP, Woods RF** (1983) The effects of aspirin and polyacrylic acid on the multiplication and spread of TMV in different cultivars of tobacco with and without the N-gene. Phytopathol Z **107**: 224–232
- 26. Yalpani N, Silverman P, Wilson TMA, Kleier DA, Raskin I (1991) Salicylic acid is a systemic signal and an inducer of pathogenesis-related proteins in virus-infected tobacco. Plant Cell 3: 809–818

**Print Edition** 

# SURS '1' TURI GOLF COURSE SUPERINTENDENTS ASSOCIATION



# RIGCSA Scholarship & Research Tournament Continues to be a Success!

The Scholarship and Research Committee sponsored another successful event with the 31st Annual Scholarship & Research Tournament held at Potowomut Golf Club on October 7th.

Organizing this event requires dedication and hard work of the committee members and staff early in the year to achieve rewarding results. Recognition goes out to the entire S&R Committee. The committee also extends a special thank you to Julie Heston for her assistance, dedication and strong administrative support.

To our annual sponsors, who play a key role in the tournament's success, the committee extends its grati-

Pictured above (L-R): Mark Marcantonio, Potowomut Club President; Patrick Gertner, CGCS, Potowomut GC Superintendent; John Eidson and Pat Hogan

tude. Please see the full list of sponsors for this event on the following pages.

Special recognition is also extended to Patrick Gertner, CGCS and the entire team at Potowomut Golf Club. The superb conditions of the course and the facility coupled with excellent service provided by the staff greatly contributed to the day's success.

In closing, the unconditional support and efforts of all participants will allow the Scholarship & Research Tournament to remain a key event representing the RIGCSA's strong commitment to educational enhancement.

Sincerely, *Richard Lombardi, Chairman*Scholarship and Research Committee

Inside this Issue:	
President's Message	2
Kevin Doyle's GCSAA Corner	3
Phosphorous vs. Phosphite	4
S&R Tournament Photos	6
S&R Tournament Sponsors	7
September Meeting Photos	11
Member News	12

#### RIGCSA Board of Directors

President
Michael Whitehead, CGCS
Pawtucket Country Club
(508) 761-7657

Vice President
Nicholas Burchard
Crestwood Country Club
(508) 336-8582

Treasurer
Andrew Cummins
Agawam Hunt
(401) 434-0980

Secretary
William Coulter, CGCS
Swansea Country Club
(508) 379-9741

Director Patrick Hogan SODCO (800) 341-6900

Director Christopher Coen Newport Country Club 401-847-5903

> Director Thomas Hoffer Lake of Isles (860) 625-0145

Past President Jerry Noons The Back Nine Club (508) 947-9991

Newsletter Editor
Joe Oliveira
Green Valley Country Club
(401) 848-7520

Chapter Executive
Julie Heston
phone: (401) 934-7660
fax: (401) 934-9901
jheston@verizon.net
www.rigcsa.org

# President's Message



In my newsletter message back in June I lamented that we just never seem to get long stretches of good weather anymore. After the record rains in June and the devastating heat waves of July took

their toll, the weather moderated nicely and things got back to normal for most of us. At least where I am, this September and October had some of the finest weather for growing turf and playing golf that I can recall. I hope all of you have been able to breathe a sigh of relief, and found the time to get out and do the things you like to do when away from work. We have all earned it this year.

About the only day in the past two months that the weather wasn't cooperative was at the RIGCSA Championship held at Carnegie Abbey. Dean Chase and his staff had the course primed and ready for us, but torrential rain washed out any hope of completing the round. I know Dean and Mike Godet were disap-

pointed with the turn of events, but we appreciate their efforts and extend our thanks.

Thanks also go out to Patrick Gertner, CGCS for hosting the 31st Annual Scholarship and Research Tournament at Potowomut Golf Club. The blustery winds made for a challenging day of golf, but Patrick and his staff did a nice job of setting the course up to be demanding yet fair. The food was tremendous and the Pro Shop staff took excellent care of us.

I would also like to thank all of our members who played in the S&R or made donations this year. The continued support helps insure that our fine association will lead the way in assisting students and turfgrass researchers for many years to come.

Sincerely, Mike Whitehead, CGCS RIGCSA President

#### **Scholarship Applications are Now Available**

Please visit www.rigcsa.org for an application

OI

contact Julie Heston (401) 934-7660 or jheston@verizon.net

To have an application mailed or emailed to you.

Deadline to submit applications is

December 3, 2013

Scholarships will be awarded at the Annual Meeting in January 2013.

## **Kevin's GCSAA Corner**

#### By Kevin Doyle, GCSAA Northeast Field Rep.



Perhaps you have seen the emails floating around your inbox: "Volunteers needed!" Most of you probably just delete that one, right? Well, perhaps you might be willing to reconsider. In a year and a half in my new position, I have volunteered at four events, and am leaving in two days to make it five. Why do I volunteer you might ask? Well, I am almost certain my reasons would be similar to yours when you break it down. For

those of you that have worked on a staff hosting a large scale event or volunteered as part of one, I'd like to hear feedback if my assessment is off the mark. If you have never volunteered for an event, perhaps you might want to try after reading about it?

#### Why?

In short, why not! The facility, our colleague and often our friend, is looking to put its best foot forward, not just once, but for an extended period of time. Challenge the competitors, impress a world-wide audience, or attain member satisfaction, whatever the specific reason, achieving these lofty conditions take an immense amount of labor. Whether a facility operates with a crew of twenty or sixty, extra help is always needed. What kinds of tasks are needed to be done? Anything and everything are on the table, and the skill set can vary from simply filling divots, to walk-mowing or rolling greens. All duties are not the same. Fluffing rough (standing up four inch rough around greens with a fan rake) can be a work-out, while towing a turbine to blow debris off fairways isn't exactly going to work up a sweat, so physical demands should not hold you back. The long and short of it is, when the tasks are complete and the first ball is struck to begin play, you have helped bring a facility as

close to perfection as possible. That is a great feeling! Who?

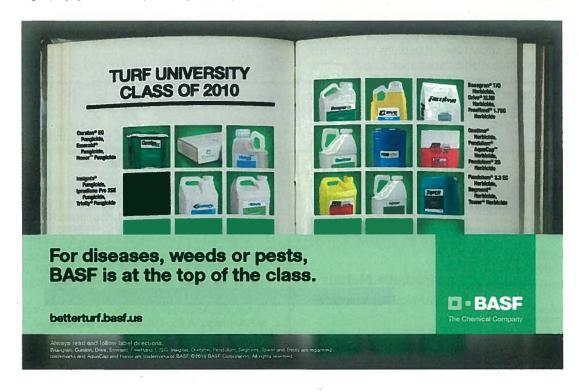
The volunteer staffs I have been with are a mix of affiliates, superintendents, assistants, interns and regular staff from courses near and far. Learning what happens inside the ropes to make events a success has great value, especially to students and assistants. Superintendents and affiliates can often use these opportunities to further build relationships. In short, anyone can benefit from volunteering.

#### Will Work for Food!

Probably a better way to phrase the above: What do I get out of it? They seem to feed the volunteers <u>very</u> well. Often, a uniform is part of the package, so a nice golf shirt or other swag might be part of the deal. Your volunteer badge allows access to the event, so you might see some of the best athletes competing at the highest level while you are there. Above all, I've found that it is fun! The business of perfection is extremely serious, but the conversation and interaction with your peers can make for a very enjoyable experience.

This year was a particularly busy year in the Northeast region for large-scale events. The need for volunteers was greater this year with the U.S. Amateur, U.S. Open, U.S. Women's Open, Walker Cup, and PGA Championship all making appearances in the area. If you didn't have the chance to get inside the ropes there, there are many annual opportunities as well with the Deutche Bank Championship, The Barclay's, Dick's Sporting Goods Open, CVS Charity as well as others. If you have volunteered in the past, I hope you have found it as rewarding as I have and will consider lending a hand again. If you

continued on page 5



## Phosphorous vs. Phosphite

In order to fully understand the differences let's start by clearing up the differences between phosphorous fertilizers (P) and phosphite fertilizers. Fertilizer P is normally found in the form of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). In acid soils, fertilizer P is converted primarily into the dihydrogen phosphate (H<sub>2</sub>PO<sub>4</sub>) form. This form is readily taken up by the host plant or it reacts with Fe, and or Al and is tied up in the soil. Common examples of fertilizer P are monammonium phosphate, (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) and of course Nutrol, monopotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>).

PhosphorouS Acid (H<sub>3</sub>PO<sub>3</sub>) appears only slightly different than phosphoriC acid (H<sub>3</sub>PO<sub>4</sub>). It has one less oxygen attached to phosphorous. Phosphorus acid can be altered and become a phosphonate ion (HPO<sub>3</sub><sup>2</sup>). Once it is in the phosphite form, it is very stable and does not convert to the fertilizer P form, phosphate. The phosphonate ion is more commonly referred to as phosphite. Since phosphite has one less oxygen molecule than phosphate (H2PO4) it is more soluble and quickly absorbed by the plant. The plant does not recognize phosphite as a nutrient source and it is xylem and phloem active. It is interesting to note that fosetyl-Al which is monoethyl phosphonate also converts to phosphite in the plant and becomes a true systemic fungicide.

Phosphites have been investigated for potential use as a fertilizer. They reported P-deficiency symptoms when using phosphorous acid (phosphite) as a nutrient for plant growth. Whereas, P fertilizer (MAP) is an excellent plant nutrient but is unable to control Pythium aside from making the host plant healthier, Forster et al. (1998). It is believed that the primary function of phosphite is to stimulate the plants natural defenses by accumulating high levels of antibiotic compounds called phytoalexins. In turn, the plants metabolism and cell wall thickness improves. Recent studies have shown that phosphite applications inhibit spore germination and penetration into the plant, by blocking mycellial growth and spore production. Others have observed an increase in the host plants natural defenses against several Pythium invaders and significantly altering summer stress.



(401) 835-0287 Cell (413) 863-0099 Fax

Michelle@AtlanticGolfandTurf.com

9 Industrial Boulevard Turners Falls, Massachusetts 01376 www.AtlanticGolfandTurf.com

Michelle Maltais

**Technical Representative** 

Many phosphite products exist in the market today. They can be separated into different groups based on how they are manufactured. Potassium phosphites for example, comprise the largest group. Phosphoric acid and potassium hydroxide are combined together in an acid base heat evolving reaction to create potassium phosphite (K<sub>3</sub>PO<sub>3</sub>). This group can be further separated based on phosphite load per gallon.

When urea is combined with phosphorous acid a urea phosphite is created. It's a simple reaction creating a stable form of phosphite. This formulation has a very high phosphite load.

Understanding the product pH, the rate of application and water pH is vital. For Example, 0-0-25 potassium thiosulfate has a pH of approximately 8.0. The rate ranges from 6 - 11 oz/1000 sf. The 150 gallon tank covers approximately two acres of turf, 2 - 7.5 gallons of 0-0-25 will be added to the tank. The pH of the spray tank will rise above a pH of 7.0 creating an alkaline spray mixture. Alkalinity creates chemical breakdown of organophosphates, carbamates, trinexapac-ethyl and etc.. It is recommended to keep your spray tank pH between 4-6.

The general rule historically has been to follow the W-A-L-E method which is:

- 1. Fill tank with water, at least half full
- Add WP's and or WDG's
- 3. Agitate until they are completely dispersed continue filling to 90% capacity
- Add flowable liquids
- 5. Add EC's and or PHOSPHITES or Fosetyl-Al, filling tank to 100% capacity

Scott Mackintosh Atlantic Golf & Turf

#### References:

Fenn, M.E., and Coffey, M.D. 1985. Further evidence for the direct mode of action of Fosetyl-Al and phosphorous acid. Phytopathology 75:1064-1068.

Förster, H., J.E. Adaskaveg, D.H. Kim, and M.E. Stanghellini. 1998. Effect of Phosphite on Tomato and Pepper Plants and on Susceptibility of Pepper to Phytophthora Root and Crown Rot in Hydroponic Culture.Plant Dis.82:1165-1170.

Handbook of Phytoalexin Metabolism and Action, edited by M.Daniel&R.P.page 305-306 Copy right 1995 by Marcel Dekker, Inc. 270 Madison Avenue, New York, New York

Fungicidal Activity and Nutritional Value of Phosphorous Acid.Brunnings, A.M., Datnoff, L.E., and Simone, E. H.

#### Kevin Doyle - continued from page 3

have never stepped to the plate to help out, I recommend you try it. You never know what golfers might do when you put a collection of superintendents together in search of perfection....possibly make history!

#### **GCSAA Resources and Deadlines**

Hopefully, this section will serve as a reminder of benefits you receive already but forgot, or highlight new benefits beyond the award winning magazine you already receive!

All eligible members are automatically enrolled into the dues term life insurance group policy at no additional cost! Benefits range from \$1000-10,000 depending on the age of the member. For specifics on this member benefit visit GCSAA.org and click on "Membership & Benefits" near the top of the page. Be sure to visit if you need to update your beneficiary.

**Golf Industry Show:** 

Housing for the 2014 Conference and Show in Orlando is now open! Reserve your housing early before they fill up. Conference Registration for Members opens November 5<sup>th</sup>. Details, including changes to the 2014 show and highlights from 2013 can be found here.

**Bayer Plant Health Scholarship** 

Two Class A and superintendent members of GCSAA will each receive a \$2,500 award for continuing education in the area of plant health. The award can be used in the following ways:

Toward costs for continuing education at an institution of

higher learning. A check will be issued to both the scholarship recipient and the institution.

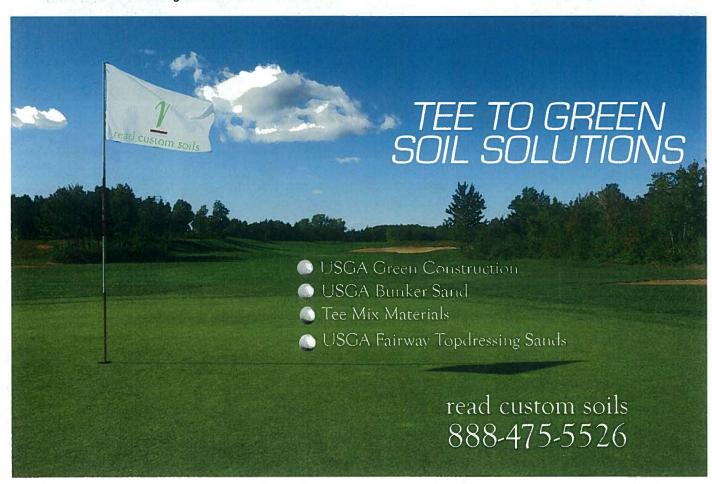
Toward costs for attending a local, regional or national educational conference or workshop for the purpose of continuing education. The award check will not have taxes withheld for federal or state purposes. Recipients choosing this option will receive Form 1099 from GCSAA in 2014 stating the value of the package based on actual costs, which they will report as other income for 2013. Please consult a tax adviser with any questions.

Application deadline has been extended to November 1, and more information can be found here.

\*\*\*\*\*\*Look for an exciting new communication tool from GCSAA coming soon.....and I have been working with an industry partner on a program to benefit chapter education programs!

Again, if I can be of any assistance, please feel free to contact me.

Kevin Doyle
GCSAA Field Staff
kdoyle@gcsaa.org
Follow me on Twitter @GCSAA\_NE



# RIGCSA Scholarship & Research Tournament





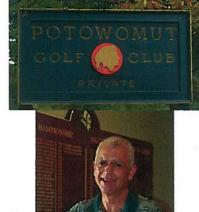


























# RIGCSA 31st Annual Scholarship & Research Tournament Sponsors

#### **Super Titanium**

(\$1000.00 or up)

BASF Turf & Ornamental
Bayer Environmental Science
Rhode Island Golf Association
Syngenta Professional Products
Valent Professional Products

#### **Platinum Plus**

(\$700.00 - \$999.99)

Agrium Advanced Technologies
Harrells

#### **Platinum**

(\$300.00 - \$699.00)

A-OK Turf Equipment
Barenbrug USA
Country Club Enterprises
New England Golf Cars
Shrewsbury Landscapes Inc.
Tartan Farms, LLC
Turf Enhancement Enterprises
Turf Products Corporation
United Phosphorus, Inc. (Phoenix)
WinField Solutions

# RIGCSA 2013 NEWSLETTER SPONSORS

#### AGRIUM ADVANCED TECHNOLOGIES Direct Solutions

Fertilizer, Seed, Chemicals Jim Pritchard (401) 258-5472 jpritchard@agriumat.com Mike Santos (401) 793-1639 msantos@agriumat.com

#### **ALLENS SEED**

(401) 294-2722 (800) 527-3898
Celebrating over 60 years of servicing
Golf Course Superintendents with products
for managing quality turfgrass. When you
need fertilizer, control products, premium
grass seed, equipment repair and parts call
Adam Allen, Al LaPrise,
Erik or Paul Hagenstein, or Peter Lund for
more information.

#### A-OK TURF EQUIPMENT

Lastec, Tycrop, Blec, Wiedenmann, Therrien, Graden, Sweep & Fill, Baroness, and used equipment. (401) 826-2584 www.aokturfequipment.com

#### **BARENBRUG USA**

Producers of RTF, Turf Blue HGT, Supercharged Bentgrasses and Regenerating Perennial Rye Great in Grass Bruce Chapman, Territory Manager 401-578-2300 bchapman@barusa.com

#### BASF TURF & ORNAMENTAL

"We don't make the turf. We make it better." betterturf.basf.us

#### **BAYER ENVIRONMENTAL SCIENCE**

Building on an already solid foundation of proven products to help you succeed Brian Giblin (508) 439-9809 Brian.Giblin@bayer.com Baked by Bayer

#### **BISCO / RAIN BIRD GOLF**

Irrigation Sales Andrew Langlois (508) 868-6996 Jay Anderson (203) 494-5217 Dan Fuller (508) 789-2323

#### THE CARDINALS, INC.

John Callahan (800) 861-6256 Complete distributor of golf course accessories; seed, fertilizer, chemicals, wetting agents, safety supplies and other turf related specialty products.

# RIGCSA 31st Annual Scholarship & Research Tournament Sponsors

#### Gold

(\$250.00 - 299.00)

Arysta Life Science DAF Services, Inc. Read Custom Soils TLC-Products

#### <u>Silver</u>

(\$200.00 - \$249.00)

Allens Seed
Atlantic Golf & Turf
BISCO
The Cardinals, Inc.

Chas. C. Hart Seed Co.
DGM Systems / Kochek
Five Star Golf Cars
Hillcrest Turf Services
Mulligan's Island Golf & Ent.
New England Specialty Soils
Northeast Nursery
Shawnmark Industries
Slater Farms

SODCO, Inc. Steven Willand Inc. Tom Irwin, Inc.

#### **Golf Balls**

**Acushnet Company / Titleist** 

#### **Flags**

John Deere Golf - Ron Tumiski

#### **Outside Sponsors**

Arnold Lumber Company
Dave's Bar & Grill
Grigg Brothers
John J. Clark Insurance Inc.
McLaughlin & Moran, Inc.
Patrick Fallow (1996 Scholarship Recipient)
RI Turfgrass Foundation
Security Cleaners
UBS Financial Services

# RIGCSA 2013 NEWSLETTER SPONSORS

THE CHAS. C. HART SEED CO. (800)-326-4278 www.HARTSEED.com

Mike Carignan Cell: 603-540-2562

mcarignan@hartseed.com
Independent distributor of quality turfgrass
seed, fertilizer and Turf care products. Authorized distributor for Bayer, Syngenta,
Aquatrols, Griggs Bros.

#### **COUNTRY CLUB ENTERPRISES**

Club Car Utility Vehicles and Golf Cars Sales - Service - Parts www.ccegolfcars.com (800)-662-2585 Keith Tortorella 508-982-4820 Mike Turner 508-245-1268

#### GARDNER + GERRISH, LLC

Golf Course Design

Offering over 15 years of golf course design experience including; feature renovation, tree analysis, cart path layout, master planning, construction observation, planting design and landscape architecture.

Contact RIGCSA member Tim Gerrish, RLA at 401-263-3784 tim@gardner-gerrish.com

#### HARRELL'S

(401) 397-5500

Service - Knowledge - Experience
The superintendents' source for high-tech turf
care products, contact Michael Kroian.

#### HILLCREST TURF SERVICES

Providing quality service to golf courses dethatching, root pruning, seeding Michael Parks 617-852-0479 michaelparks09@comcast.net

#### MATRIX TURF SOLUTIONS LLC

Distributor of Quality Fertilizer, Grass Seed and Control Products for the Golf Course and Landscape Industry. Larry Anshewitz 508-789-4810 Chris Bengtson 978-360-0981 Mike Pajolek 508-789-1529

#### **NEW ENGLAND GOLF CARS**

Sales, Service, Rentals

Scott Cookson, Paul Amorin, Jon Cookson (508) 336-4285 Fax: (508) 336-4762 www.NewEnglandGoffCars.com Yamaha Goff Cars / Yamaha Utility Cars

#### **NEW ENGLAND SPECIALTY SOILS**

1mm & 2mm. Top Dressing Sand Rootzone Mixes, Buff & HD Bunker Sand Divot Blends- Bulk/Bagged delivery Ed Downing 978-230-2300 ed@nesoils.com

# Scott Gabrielson Renews Professional Certification

Scott W. Gabrielson, GCSAA certified golf course superintendent at Alpine Country Club, Cranston, R.I., has completed the renewal process for maintaining his status as a Certified Golf Course Superintendent (CGCS) with the Golf Course Superintendents Association of America (GCSAA).

Gabrielson has been at Alpine Country Club since 2002. An 18-year GCSAA member, he initially achieved his certification in 2010. Approximately 1,500 golf course superintendents worldwide currently hold "CGCS" status.

According to GCSAA Chief Executive Officer Rhett Evans, "25 percent of GCSAA's Class A members have elected to earn the highest level of recognition through the professional designation "CGCS" by completion of the GCSAA Certification Program. This program requires their demonstration of a higher set of competencies in golf course management through testing and practical application. Employers can be confident they employ a career professional who will increase their chances of having consistently superior course conditions."

To qualify for GCSAA's new competency-based certification program, a candidate must have at least three years experience as a golf course superintendent, be employed in that capacity and meet post-secondary educational requirements and/or continuing education points. The candidate's knowledge, skills and abilities are validated through the development of a portfolio consisting of their responses to skill statements, case-study scenarios and submission of work samples; an on-site inspection of their golf facility; and a rigorous sixhour examination covering: equipment, irrigation systems, materials and technology; golf course and grounds; human resources, rules of golf, financial and administrative systems, regulatory and programmatic systems, crisis management, project management and ethics and values.

Maintaining certified status requires renewal every five years after the initial date of certification. To fulfill certification renewal requirements, a candidate must participate in 150 hours of continuing education and professional development.

#### **Bayer Environmental Science**

BACKED by BAYER...

Building on an already solid foundation of proven products to help you succeed.

**Brian Giblin** 

# RIGCSA 2013 NEWSLETTER SPONSORS

#### PLANT FOOD COMPANY, INC.

The Liquid Fertilizer Experts and Perfectionists Like You Jason Dowglewicz 860.508.5419 / 800.562.1291 idowg@plantfoodco.com www.plantfoodco.com

#### SHAWNMARK INDUSTRIES, INC.

"TOMORROW'S Chemical Needs TODAY"A complete line of specialty turf products as well as engine degreasers, equipment maintenance products, aerosols and ice melt. Call Matt Howland at (401) 295-1673 for personalized service 24 hours a day or visit our website at www.shawnmark.com.

#### STEVEN WILLAND INC.

George Wise - 508-274-7445 Eric Euell - 401-640-5031 Parts and Service - 866-435-1380 www.stevenwillandinc.com

### SYNGENTA PROFESSIONAL PRODUCTS

Melissa Gugliotti 860-221-5712 Email: Melissa.gugliotti@syngenta.com www.syngentaprofessionalproducts.com

#### TOM IRWIN, INC.

1-800-582-5959

Greg Misodoulakis - 508-243-6166

New England's most complete distributor of chemicals, Lebanon fertilizers, Earthwork's organics, seed and golf course supplies.

With Tom Irwin, you're not alone.

#### TUCKAHOE TURF FARMS, INC.

(800)-556-6985
Offering a selection of putting green quality bentgrass varieties. Also, blends for tees, fairways, bunkers and roughs.
Washing available.
Contact Steve Donohue or Joe Farina.

#### TURF ENHANCEMENT ENTERPRISES

Tom Fox 508-450-9254
Featuring Floratine Products,
Analync Soil Testing and Analysis,
JRM tines and bedknives and
Greenleaf TurboDrop spray nozzles.

#### TURF PRODUCTS CORPORATION

(800)-243-4355

Carrying the complete line of TORO equipment. Call Dana Dubois for demonstrations. For your TORO irrigation needs - sprinklers, pipes, fittings, Otterbine aerators and wire trackers, contact Tim Berge.

# THE MOWER THEY DON'T WANT YOU TO SEE.



The competition doesn't want you to see the JACOBSEN ECLIPSE 322 riding greens mower. They can't match its ZERO LEAK POINTS. They cant offer PROGRAMMABLE FREQUENCY-OF-CLIP from an LED screen. They can't provide INDIVIDUAL REEL CONTROL. And they can't get anywhere near the TRUE HYBRID FUEL SAVINGS or LEGENDARY QUALITY-OF-CUT. When it comes to the ECLIPSE 322, the competition can't do anything except hope you don't see it. I guess we just ruined that for them, too.

Turfco--Ventrac--Smithco--RedMax--Redexim--Planet Air

## **September Meeting Photos - Carnegie Abbey Club**























- Bunker Sand
- Root Zone Blends Green Divot Mixes
- Bridge Sand
- Drainage Stone . Drill and Fill
- Synthetic Turf
- Planting Mixes
- Green Rooftops - Blend to YOUR Ratio

We provide the highest quality natural sands and stone products. For applications ranging from sports turf fields to golf courses, our products are perfect for every project.

Let us quote on your project. Call Bob Chalifour at 860-908-7414, or fax all specs to us at 401-762-4976.





Slatersville, RI 02876 401-766-5010 www.hollistonsand.com



Our products are also available dry and in bulk and packaged form. Delivered with dump truck, flatbed or pneumatic tanker.

## **MEMBER NEWS**

#### **Announcements:**

Congratulations to Eric and Lindsay Euell on the birth of their daughter Lila who was born on October 23, 2013.

Our condolences are extended to John Petraitis and family on the passing of his wife Claire who passed away on September 25, 2013.

Our condolences are extended to Debbie and David Creta on the passing of Debbie's mother, Ethel Giusti, on September 30, 2013.

Larry Anshewitz has new contact information. His email address is <a href="mailto:lanshewitz@comcast.net">lanshewitz@comcast.net</a> Cell phone: 508-789-5357 Home: 508-977-9871

John Bresnahan has accepted a new position as Strategic Market Support Manager for Harrells. His new email address is <a href="mailto:ibresnahan@harrells.com">ibresnahan@harrells.com</a> and his phone numbers stay the same at office -413.565.5340 and mobile 413.374.4102.

Mike Pajolek is now working for WinField Solutions. His new email address is mcpajolek@landolakes.com. His phone number is the same at (508) 789-1529.

Chris Bengtson is now working for WinField Solutions. His new email address is crbengtson@landolakes.com. His phone number is the same at (978) 360-0981.

BISCO is pleased to announce that Bill Stinson has joined BISCO as Golf Manager, effective September 9, 2013. Bill brings with him nearly twenty years of experience in golf irrigation. He also has extensive experience with the Rain Bird product line, pumping, and the many allied products used in golf course irrigation. Bill is based in western MA, with easy access to all locations in New England. He can be reached at: 413-668-7943 or bstin-

son@biscoirrigation.com

The Golf Course Superintendents Association of America (GCSAA) has awarded its **2013 Joseph S. Garske Collegiate Grants** to Kristen Sauer, Catherine Felicetti, Christopher McAvoy, Samantha Bradley and Kaci Whitehead.

The Garske Grant was established in honor of Par Aide company founder Joseph S. Garske. It is funded by Par Aide, a golf course accessory company, and administered by the Environmental Institute for Golf, the philanthropic organization of GCSAA. The program assists children and stepchildren of GCSAA members to fund their education at an accredited college or trade school with one-time, one-year grants awarded to five winners without renewals. Grants are based on community service, leadership, academic performance and a written essay.

- Sauer, from Boylston, Mass., is a student at Providence College and earned a \$2,500 scholarship.
   Her father, Todd A. Sauer, is the GCSAA Class A superintendent at Mount Pleasant Country Club in Boylston, Mass.
- Felicetti, an Ithaca College student from Forestdale, Mass., earned a \$2,000 scholarship. Her father, Joseph F. Felicetti, is the GCSAA certified golf course superintendent at The Pinehills Golf Club in Plymouth, Mass.
- McAvoy, a Fordham University student from West Hempstead, N.Y., earned a \$1,500 scholarship. His father, Thomas O. McAvoy, is the GCSAA certified golf course superintendent at Old Westbury Golf & Country Club in Old Westbury, N.Y.
- Bradley, a University of St. Joseph student from Plainville, Conn., earned a \$1,000 scholarship. Her father, Gregory Bradley, is the GCSAA Class A superintendent at Farmington Woods Country Club in Unionville, Conn.
- Whitehead, an Indiana University/Purdue University of Fort Wayne student from Syracuse, Ind., receives a \$500 scholarship. Her father, James B.
   Whitehead, is the GCSAA member superintendent at Maxwelton Golf Course in Syracuse, Ind.

THAO + YAMAKAWA

#### **REVIEW ARTICLE**

# Phosphite (phosphorous acid): Fungicide, fertilizer or bio-stimulator?

#### Hoang Thi Bich THAO1 and Takeo YAMAKAWA2

<sup>1</sup>Plant Nutrition Laboratory, Division of Bioresource and Bioenvironmental Sciences and <sup>2</sup>Plant Nutrition Laboratory, Department of Plant Resources, Faculty of Agriculture, Kyushu University, Fukuoka 812-8581, Japan

#### **Abstract**

Phosphite (PO<sub>3</sub><sup>3</sup>; Phi), a reduced form of phosphate (PO<sub>4</sub><sup>4</sup>; Pi), is widely marketed as either a fungicide or fertilizer or sometimes as a biostimulant. This is confusing for both distributors and growers. The present paper explores data from various studies to clarify that Phi does not provide plant P nutrition and thus cannot complement or substitute Pi at any rate. In addition, Phi itself does not have any beneficial effect on the growth of healthy plants, regardless of whether it is applied alone or in combination with Pi at different ratios or different rates. The effect of Phi on plants is not consistent, but is strongly dependent on the Pi status of the plants. In most cases, the deleterious effect of Phi is evident in Pi-starved, but not Pi-sufficient, plants. Plants fertilized with Pi allowing for approximately 80–90% of its maximum growth might still be at risk of the effect. This negative effect becomes more pronounced under more seriously Pi-deficient conditions. Although a number of studies have shown positive crop responses to Phi, these responses are likely to be attributable to the suppression of plant diseases by Phi and/or to Pi formed from oxidation of Phi by microbes. In addition, indirectly providing P by Phi-to-Pi oxidation is not an effective means of supplying P to plants compared with Pi fertilizer. An understanding of these issues will aid the right selection of fertilizer as well as minimize the harmful effects of Phi use on crops.

Key words: biostimulant, fertilizer, fungicide, phosphate, phosphite.

#### INTRODUCTION

Phosphorus (P) is one of the major essential macronutrients required by all living organisms. In nature, P does not exist as a free element, but rather in combination with other elements, such as oxygen (O) or hydrogen (H). It occurs in a fully oxidized form (P has valence of +5) as phosphate anion (PO<sub>4</sub><sup>3-</sup>; Pi) and with one less oxygen (P has valence of +3) as phosphite (PO<sub>3</sub><sup>3-</sup>; Phi). The conjugate acid of the phosphite anion is phosphorous acid (H<sub>3</sub>PO<sub>3</sub>). In general, the term phosphite is commonly referred to as the salts of phosphorous acid and the term phosphonate is used to mean phosphite ester containing a carbon–phosphorus (C–P) bond that is chemically distinct from the labile carbon–oxygen–phosphorus (C–O–P) bond found in phosphate ester (White and Metcalf 2007).

Correspondence: H. T. B. THAO, Plant Nutrition Laboratory, Division of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan. Email: tb\_hoang@yahoo.com

Received 3 September 2008.

Accepted for publication 25 December 2008.

For many years, Pi compounds were considered to be the only form that could supply P nutrition to plants. In fertilizer, P is normally found in the form of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and its salts, such as, triple super phosphate, ammonium phosphate and potassium phosphate. All of these forms readily disassociate to release hydrogen phosphate (HPO $^{2}$ ) and dihydrogen phosphate (H<sub>2</sub>PO $^{2}$ ), which are used by plants. Phi compounds have been recognized as excellent fungicides for controlling many important plant diseases caused by Oomycetes, particularly Phytophthora sp. (Fenn and Coffey 1984; Foster et al. 1998; Grant et al. 1992; Guest and Grant 1991; Guest et al. 1995; Jackson et al. 2000; Jee et al. 2002; Smillie et al. 1989). However, they are not considered to be P fertilizers because an early study examining different P compounds by MacIntire et al. (1950) concluded that Phi compounds were a very poor source of P for crops compared with Pi fertilizers. Renewed interest in Phi as a plant nutrient has increased since the early 1990s when Lovatt (1990a) discovered that P deficiency caused changes in nitrogen metabolism and that the foliar application of potassium phosphite to P-deficient citrus recovered the biological response of plants and

Table 1 From fungicides to fertilizers: the marketing of some products with phosphorous and phosphite as the active ingredient

Product	Company	Country	Active ingredient	Marketed as
Aliette	Bayer Cropscience	Germany	Aluminum phosphite	Fungicide
Nutri-phite	Biagro Westem Sales	USA	Phosphite and organic acids	Fertilizer
Ele-Max	Helena Chemical	USA	Phosphorous acid	Foliar fertilizer
ProPhyt	Luxembourg-pamol	USA	Monopotassium phosphite	Systemic fungicide
Nutrol	Lidochem	USA	Potassium phosphite	Fertilizer and fungicide
Phostrol	NuFarm America	USA	Phosphorous acid	Biochemical pesticide
Agrifos	Liquid Fert Pty (Agrichem)	USA	Monopotassium phosphite	Fungicide
Foli-r-fos 400	UiM Agrochemicals	Australia	Monopotassium phosphite	Fungicide
Fosphite	Jh Biotech	USA	Monopotassium phosphite	Fungicide
Lexx-a-phos	Foliar Nutrients Inc	USA	Monopotassium phosphite	Fungicide
Trafos line	Tradecorp	Spain	Potassium phosphite	Fertilizer and defense stimulator
Phytos'K	Valagro	Italy	Potassium phosphite	Biostimulant (registered
				as EC fertilizer)
Phosfik line	Biolchem	Italy	Phosphorous acid	EC fertilizer
Fosfisan, Vigorsan	Agrofill	Italy	Potassium phosphite	Defense stimulator (registered as fertilizer)
Geros-K	L-Gobbi	Italy	Potassium phosphite	EC fertilizer
Kalium Plus	Lebosol	Germany	Potassium phosphite	EC fertilizer
Frutoguard	Spiess Urania	Germany	Potassium phosphite	EC fertilizer
Foliaphos	Plantin	France	Potassium phosphite	EC fertilizer

Source: Leymonie 2007. EC, European Commission (for identifying chemicals).

consequently restored normal plant growth. Additional studies by Lovatt (1990b) further suggested that soil or foliar application of Phi could replace Pi as a source of P in avocado. A series of US patents, such as US Patent numbers 5514200 (Lovatt 1996), 5830255 (Lovatt 1998) and 5707418 (Hsu 1998) describe formulations containing Phi that are suitable as P fertilizers for plants. The work of Lovatt led to the first commercialization of Phi compounds as fertilizer. This fertilizer was sold under the trademark Nutri-phite (Biagro Western Sales, Visalia, CA, USA). Many new P fertilizers based on Phi are now being marketed. The list of Phi products that are available in the American and European markets that are sold as fertilizers now includes 10 different brand names (see Table 1) (Leymonie 2007). All of these products are formulated as alkali salts of phosphorous acid (H<sub>3</sub>PO<sub>3</sub>) and have been registered under the fertilizer laws. Some are even described more as "biostimulants" than as fertilizers. However, the representation and the use of Phi-containing products as sources of plant nutritional P have been subjected to ongoing controversy. This has also created much confusion for distributors and growers (Leymonie 2007). There are numerous publications indicating that Phi can be well absorbed by leaves and roots, but has no utility for plants as a P fertilizer (Carswell et al. 1996; Forster et al. 1998; Schroetter et al. 2006). Instead, Phi was found to have negative effects on the growth and metabolism of Pdeficient plants by suppressing the typical molecular and

developmental responses of plants to P deficiency (Abel et al. 2002; Carswell et al. 1996, 1997; Ticconi et al. 2001; Varadarajan et al. 2002). Phi intensifies the deleterious effects of P deficiency by tricking Pi-deprived plant cells into sensing that they are Pi sufficient, when in fact their cellular Pi content is extremely low (McDonald et al. 2001a).

The confusion about Phi became greater when some scientists (Lovatt and Mikkelsen 2006; Watanabe 2005) claimed that the negative effects of Phi on plant growth observed in many studies resulted from the inappropriate use of this material, for example, as a primary source of P or in excessive amounts. Lovatt and Mikkelsen (2006) emphasized that "since phosphite is chemically different from phosphate, these differences must be taken into consideration to avoid plant toxicity" and that Phi, if used at appropriate rates, can provide stimulation to plants that may not occur with Pi. Lovatt and Mikkelsen (2006) suggested that Phi is more than just a fungicide; for example, it increases floral intensity, yield, fruit size and total soluble solids. In addition, combinations of Phi and Pi ions are believed to be more effective than either Pi or Phi alone in plant assimilation (Foster et al. 1998; Young 2004).

What are the true effects of Phi on the growth of plants aside from the fungicidal actions? Does Phi have any nutritional impact on plants? Can Phi provide stimulating effects to healthy plants? Can a combination of Phi and Pi be more effective in plant assimilation than either ion

alone? This article will explore data from various studies to shed light on these questions.

#### PHOSPHITE IS NOT A FERTILIZER AND DOES NOT HAVE ANY BENEFICIAL EFFECT ON THE GROWTH OF HEALTHY PLANTS

Aside from the early works of Lovatt (1990a,b) demonstrating that Phi was readily taken up through leaves and could replace Pi as a source of P in the metabolism of citrus and avocado, a number of studies have highlighted the potential use of Phi as P fertilizer for plants. Albrigo (1999) demonstrated that foliar application of potassium phosphite on Valencia orange trees in Florida clearly increased both the yield (boxes per hectare) and quality (orange juice soluble solids per hectare) over untreated controls, although the mechanism of the Phi effect remains unclear. Another study by Lovatt (1999) on Navel orange trees indicated that foliar application of potassium phosphite in May and July significantly increased the yield, fruit size and total soluble solids. The improvement in the yield and fruit quality after foliar application of potassium phosphite was interpreted as a response of citrus fruit to increased P nutrition. Similarly, foliar application of potassium phosphite has been reported to accelerate the flowers and fruit setting and, hence, significantly increase the yield of Satsuma orange compared with untreated controls or a foliar Pi treatment (Watanabe 2005). Rickard (2000) summarized studies on crop responses to commercial Phi-derived P fertilizers. Most of the studies in his review were carried out under field conditions and all results showed that soil or foliar application of Phi fertilizer consistently improved the yield and quality of many crops, such as celery, onion, potatoes, peaches, orange and cotton. However, there is no evidence that Phi can be used directly by plants as a source of nutritional P. In addition, data showing that the effectiveness of Phi-derived P fertilizer is equal to or better than that of conventional Pi fertilizers are very rare.

In contrast, numerous other studies have indicated that Phi compounds cannot be used as P fertilizer by plants. Hydroponically cultivated tomato and pepper plants treated with either commercial Phi or technical Phi (prepared from acid phosphorous and neutralized with KOH) exhibited a significant reduction in growth compared with Pi-fertilized plants (Forster et al. 1998; Varadarajan et al. 2002). A study by Schroetter et al. (2006) on maize plants indicated that foliar application of potassium phosphite did not improve the growth of maize plants in a field trial under either Pi-deficient or Pi-sufficient conditions. In his pot experiment, the growth of maize plants treated with potassium phosphite as the sole P source via either soil or foliar applications was strongly

inhibited. The negative effects of Phi ranged from stunted growth to complete death. A negative effect of Phi was also found in *Brassica nigra* seedlings grown *in vitro* (Carswell *et al.* 1996), in *Brassica napus* cell suspension (Singh *et al.* 2003), and in *Ulva lactuca* culture (Lee *et al.* 2005).

Although most plants readily absorb and translocate Phi, it does not appear to be readily oxidized or metabolized in plants (Carswell et al. 1996, 1997; Guest and Grant 1991). Instead, Phi is found to be deleterious to Pi-starved, but not Pi-fertilized plants by suppressing a wide range of the plant's responses to Pi deficiency (Carswell et al. 1996, 1997; Ticconi et al. 2001; Varadarajan et al. 2002), consequently exacerbating the deleterious effects of Pi starvation (Mcdoldnan et al. 2001a). Enhanced root growth or an increased root to shoot ratio, the hallmark of Pi stress responses, were found to be strongly inhibited by Phi in B. nigra (Carswell et al. 1996), tomato (Varadarajan et al. 2002), spinach, komatsuna and celery (Thao et al. 2008a,b; Thao and Yamakawa 2008). Pi-starvation-induced root growth (root hairs, root length and root density) in Arabidopsis was also significantly reduced by Phi treatment (Ticconi et al. 2001). In addition, Phi has been shown to prevent the acclimation of plants and yeast to Pi deficiency by specifically suppressing the expression of Pi-starvationinducible genes (Carswell et al. 1996, 1997; Mcdoldnan et al. 2001b; Ticconi et al. 2001; Varadarajan et al. 2002). Biochemical adaptations to Pi starvation include increased synthesis of anthocyanins, presumably to adjust photosynthesis light reactions to the Pi-dependent Calvin cycle, and increased synthesis of enzymes for scavenging intra-cellular and extra-cellular P (Ticconi et al. 2001). In Arabidopsis, the accumulation of anthocyanins and the activities of Pi-starvation-inducible nucleolytic enzymes (ribonuclease, phosphodiesterase and acid phosphatases) were effectively prevented by Phi (Ticconi et al. 2001). Studies on B. nigra and B. napus by Carswell et al. (1996, 1997) showed that the induction of acid phosphatase, phosphoenolpyruvate phosphatase, inorganic pyrophosphate-dependent phosphofructokinase and high affinity plasmalemma Pi translocator by Pi limitation was strongly inhibited in the presence of Phi. Similarly, Varadarajan et al. (2002) found that the expression of Pi-starvation-inducible genes, such as LePT1 and LePT2 (high-affinity Pi transporters), LePS2 (acid phosphatase) and LePS3 and TPSI1 (novel genes) in Pi-starved tomato was greatly suppressed by Phi treatment. Examination of the Phi effect on two yeast pho mutants revealed that Phi targets PHO84, a high-affinity Pi transporter and putative component of a Pi-sensor complex (McDoldnan et al. 2001b). The suppression of Pi-starvation responses by Phi was selective and was not caused by any general cellular toxicity of Phi (Albel et al. 2002)

because Phi did not affect the expression of auxininducible genes (Ticconi et al. 2001), total chlorophyll, the protein content or the activities of enzymes that are not associated with the Pi-starvation responses of plants (Plaxton and Carswell 1999). Data from yeast and plants suggest that Phi mimics Pi in signaling pathways, thereby suppressing various Pi-starvation-inducible responses and consequently intensifying the deleterious effects of Pi starvation.

Although numerous studies have highlighted the deleterious effects of Phi on plant growth, some researchers have claimed that these negative effects of Phi resulted from the inappropriate use of this material, such as the use of Phi as a sole P source or in excessive amounts (Lovatt and Mikkelsen 2006; Watanabe 2005), to further dissect the Pi-starvation responses of plants. These researchers suggested that Phi, if used at appropriate rates, can provide stimulation to plants that might not occur with Pi. Furthermore, a combination of Phi and Pi ions is believed to be more effective than either ion alone in plant assimilation (Young 2004). Forster et al. (1998) found that Phi did not perform well as a Pi fertilizer, but they did observe growth enhancement of tomato plants treated with a mixture of Pi and Phi when compared to Pi alone.

Recently, a series of studies by Thao et al. (2008a,b; Thao and Yamakawa 2008 and H. T. B. Thao et al., unpubl. data, 2008) on various crops (spinach, komatsuna, celery and lettuce) using different methods and rates of Phi application was conducted to intensively investigate the effects of Phi as well as a combination of Phi and Pi on the growth and P nutrition of plants. All of these studies were short-time experiments (approximately 1 month) conducted in a greenhouse and many of them used water culture to minimize the interfering effects of pathogens as well as Phi to Pi conversion, so that the true effects of Phi on plant growth could be assessed. The authors did not detect any beneficial effect of Phi on plant growth. When Phi was applied to the roots in combination with Pi at different Pi: Phi ratios, for the same total amount of P applied to the roots at either low or high total P levels, the growth of both spinach and komatsuna drastically decreased as the proportion of Phi increased (Thao et al. 2008a,b). These results suggested that Phi was not a substitute for Pi at any rate, and that there was no stimulating effect from any Phi-Pi combination on plant growth. Foliar application of Phi at a rate (0.05% P2O5) that ensured no damage to the plant leaves significantly increased the P and Phi contents in the plant tissues, but did not improve plant growth, and the growth of komatsuna actually decreased. In hydroponically cultivated celery, the addition of Phi at levels ranging from 0.1 to 2 mmol L<sup>-1</sup> into the nutrient solution did not improve plant growth

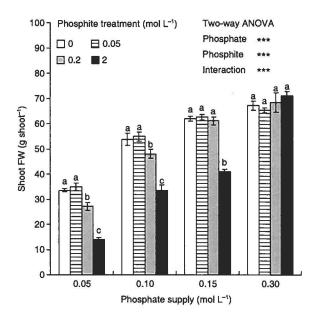


Figure 1 Effects of phosphite (Phi) treatments on shoot fresh weight (FW) of hydroponic lettuce grown under different phosphate (Pi) supplies. The Pi levels 0.05, 0.1, 0.15 and 0.3 mmol L-1 were Pi supplies for 50, 80, 90 and 100% of maximum plant growth, respectively. Error bars are standard error (n = 3). \*\*P < 0.001. Different letters indicate significant differences between means within the same Pi supply by least significant difference tests (P < 0.05). (Source: H. T. B. Thao et al., unpubl. data, 2008).

under either low (0.05 mmol L<sup>-1</sup>) or high (0.5 mmol L<sup>-1</sup>) Pi supply (Thao and Yamakawa 2008), and the growth of low Pi-fertilized celery was significantly reduced by 2 mmol L<sup>-1</sup> Phi. In lettuce (H. T. B. Thao et al., unpubl. data, 2008) the addition of Phi to the nutrient solution at different rates ranging from very low (0.05 mmol L<sup>-1</sup>) to relatively high (2 mmol L-1) substantially increased the total P and Phi in both shoots and roots, but did not improve the plant growth under various Pi supplied levels (0.05, 0.1, 0.15 and 0.3 mmol L-1 as Pi levels, respectively, for approximately 50, 80, 90 and 100% of the maximum plant growth in hydroponics) (Fig. 1). The results in lettuce further showed, regardless of the Pi level, that the addition of Phi at different rates did not have any stimulating effect on plant growth. This confirms that a combination of Phi and Pi ions is not more effective than either ion alone in plant assimilation, which is not as expected (Forster et al. 1998; Young 2004). Taken together, all these results consistently show that plants are incapable of directly using Phi as a P source and thus Phi cannot complement or substitute Pi fertilizer at any rate. Phi does not have any beneficial effect on the growth of healthy plants, regardless of whether it is applied alone or in combination with Pi at different ratios or rates. These results corroborate evidence that Phi is not really used in plants as a P fertilizer and that it has negative effects on the growth and metabolism of P-deficient plants (Carswell et al. 1996, 1997; Forster et al. 1998; Schroetter et al. 2006; Ticconi et al. 2001; Varadarajan et al. 2002).

# WHAT CONTRIBUTES TO THE POSITIVE RESPONSES OF CROPS TO PHI APPLICATION IN SOME STUDIES?

The number of products based on Phi, such as potassium phosphites, magnesium phosphites and calcium phosphites, would not have expanded in the market if there was no benefit from the application of Phi. Why some studies have shown a negative effect of Phi on plant growth (Carswell et al. 1996, 1997; Forster et al. 1998; Schroetter et al. 2006; Thao et al. 2008a,b; Thao and Yamakawa 2008 and H. T. B. Thao et al., unpubl. data, 2008; Ticconi et al. 2001; Varadarajan et al. 2002) and others have found positive crop responses to Phi (Albrigo 1999; Lovatt 1990a,b, 1999; Rickard 2000; Watanabe 2005) is not clear. It should be noted that although a number of studies have found positive crop responses to Phi, there is no evidence to date that can clearly demonstrate that plants use Phi directly as a P nutrient. We are also unaware of any plant enzyme that could oxidize Phi to Pi. To the best of our knowledge, there are no data showing a better response to Phi than to Pi of crops that are not the hosts of Oomycete pathogens. Furthermore, most studies showing positive crop responses to Phi were conducted in the field (Albrigo 1999; Lovatt 1990a,b, 1999; Rickard 2000; Watanabe 2005) where pathogens could interfere with plant growth (McDonald et al. 2001a). It is well known that Phi is able to effectively control many plant diseases caused by species of pseudofungi belonging to the order Oomycetes, particularly Phytophthora sp. (Fenn and Coffey 1984; Foster et al. 1998; Grant et al. 1992; Guest and Grant 1991; Guest et al. 1995; Jackson et al. 2000; Jee et al. 2002; Smillie et al. 1989). The fungicidal effects of Phi can act directly on the fungal pathogen and/or indirectly through stimulation of the plant defense response against pathogens (Jackson et al. 2000; Smillie et al. 1989). Thus, the benefits of Phi versus Pi in the field are likely to result from its fungicidal actions (McDonald et al. 2001a). In addition, it is now clear that various bacteria can metabolize Phi to Pi, for example, Escherichia coli, Pseudomonas stutzeri, Alcaligenes faecalis and Xanthobacter flavus (White and Metcalf 2007). Genes for the oxidation of Phi in diverse bacterial species have also been identified, such as Phn and PhoA (E. coli); Phn, htx and ptx (P. stutzeri) and htx-ptx (X. flavus). Although the process is slow and has no practical relevance (McDonald et al. 2001a), the slow release of orthophosphate by Phi-toPi conversion could contribute to the observed nutritional effects of Phi in field trials, particularly long-term trials. Thus, it is likely that the suppression of plant diseases by Phi and the indirect provision of Pi to plants after Phi-to-Pi oxidation by soil microbes are responsible for the beneficial effects of Phi on plants observed in some studies. In our recent studies (Thao et al. 2008a,b; Thao and Yamakawa 2008 and H. T. B. Thao et al., unpubl. data, 2008), under conditions to minimize the interfering effects of pathogens and Phi-to-Pi conversion, all results from various crops consistently showed that Phi does not provide plant P nutrition and does not have any beneficial effect on the growth of healthy plants, regardless of whether it is applied alone or in combination with Pi at different ratios or rates. Our results support the claim that Phi is relatively stable and is not oxidized or metabolized in plants (Carswell et al. 1996, 1997; Guest and Grant 1991).

In practical agricultural production, the application of Phi might have some positive effects on the growth and quality of plants as a result of the fungicidal properties of this material and some conversion of Phi into Pi by soil microorganisms. However, it should be kept in mind that Phi cannot be used directly by plants as a fertilizer and that Phi itself does not have any stimulating effects on the growth of healthy plants. Therefore, if the cropping environments do not have Oomycetes pathogens or if the crops are not hosts to this pathogenic group and conditions for Phi-to-Pi oxidation are unfavorable (e.g. hydroponic culture), one would expect the beneficial effect of Phi application to be negligible. Although Phi can be converted to Pi in the soil by microorganisms, this process is too slow to be agriculturally relevant compared with Pi fertilizers. The approximate half-life for Phi oxidation to Pi in soil is approximately 12-16 weeks (Adams and Conrad 1953). Furthermore, although some microbes are capable of oxidizing Phi, they preferentially use Pi over Phi as a source of P. The inoculation test of soil bacteria in a mixed culture of Phi and Pi by Adams and Conrad (1953) revealed that Phi was not used by the soil bacteria until all of the Pi in the culture was depleted and thus all traces of Pi would have been scavenged by the microbes before Phi oxidation occurred. In a study by MacIntire (1950) to evaluate the efficacy of different P compounds as P fertilizers for various crops in different soils, the application of Phi compounds was found to be very ineffective compared with Pi fertilizers. Phi was toxic to all first crops and only beneficial to the subsequent crops, highlighting the slow conversion of Phi to Pi. Recently, in 2004, farmers in South-Eastern Alabama, Southern Georgia and Northern Florida experienced toxicity problems in maize that appeared to be related to the use of ammonium phosphite, a non-conventional P fertilizer, as a starter fertilizer (Mitchell and Adams

2004). Therefore, the use of Phi as a P fertilizer is an inefficient means of supplying P to plants compared with Pi fertilizer (Lanschoot and Cook 2005; McDonald et al. 2001a).

#### THE PHYTOXICITY OF PHI DEPENDS ON THE PI STATUS OF THE PLANTS

A number of studies have emphasized the deleterious effects of Phi on Pi-deprived, but not Pi-fertilized plants (Carswell et al. 1996, 1997; Forster et al. 1998; Schroetter et al. 2006; Ticconi et al. 2001; Varadarajan et al. 2002). A recent study (H. T. B. Thao et al., unpubl. data, 2008) focusing on the effect of Phi in relation to Pi supply on hydroponic lettuce found that plants fertilized with Pi allowing for approximately 80-90% of its maximum growth were still vulnerable to Phi added to the nutrient solution at concentrations ranging from 0.2 to 2 mmol L-1 (Fig. 1). This Phi range is comparable to the dose (100 p.p.m. H<sub>3</sub>PO<sub>3</sub> equivalent to 1.2 mmol L<sup>-1</sup> Phi) recommended as a supplement into the nutrient solution for controlling Phytophthora root rot of lettuce in hydroponics (Jee et al. 2002). The severity of the Phi effect was dependent on both the Phi level and the Pi status of the plants. For example, lettuce fertilized with Pi for approximately 80% of its maximum growth or lower was still harmed by a low Phi concentration of 0.2 mmol L<sup>-1</sup>, whereas lettuce fertilized with Pi for approximately 90% of its maximum growth was only negatively affected by Phi at a high rate (2 mmol L-1); and under sufficient Pi supply (0.3 mmol L-1) the addition of Phi up to 2 mmol L-1 did not influence plant growth (Fig. 1). This result is consistent with our previous research on komatsuna and celery (Thao and Yamakawa 2008; Thao et al. 2008b), which suggested that the effects of Phi were highly dependent on the Pi status of the plants. Although plants differ in their sensitivity to Phi, the strong Pidependent effect of Phi is believed to occur in most plants. Understanding this can help to avoid the harmful effect of Phi-containing products to crops.

#### CONCLUSIONS

Our study has lead to the following conclusions:

- 1. Although Phi can be absorbed by most plants through the leaves and/or roots, it cannot be used directly as a nutrient source and therefore cannot complement or substitute Pi fertilizer at any rate.
- 2. Phi itself does not have any stimulating effects on the growth of healthy plants and Phi and Pi in combination do not provide any stimulating effects compared with Pi alone. Thus, if the cropping environment is unfavorable for Phi-to-Pi conversion and pathogens belonging to the Oomecetes group are not

- a problem, one would expect no beneficial effect of Phi on the crops.
- The effects of Phi on crops are strongly dependent on the P nutrient status of the plants. A deleterious effect of Phi was not evident in Pi-sufficient plants, but plants fertilized with Pi sufficient for approximately 80-90% of their maximum growth may still be at risk of the effect. The negative effect of Phi becomes more pronounced under more seriously Pi-deficient conditions. Therefore, Phi should not be applied to plants in sub-optimal Pi conditions.

This paper provides a clearer understanding of the effects of Phi on the growth and P nutrition of plants and will aid the selection of appropriate fertilizers as well as minimize the harmful effects of the use of Phi on crops. Our aim was to help reduce some of the confusion experienced by growers and distributors (Leymonie 2007) with regard to Phi.

#### REFERENCES

- Abel S, Ticconi CA, Delatorre CA 2002: Phosphate sensing in higher plants. Physiol Plant., 115, 1-8.
- Adams F, Conrad JP 1953: Transition of phosphite to phosphate in soils. Soil Science, 75, 361-371.
- Albrigo LG 1999: Effects of foliar applications of urea or Nutriphite on flowering and yields of Valencia orange trees. Proc. Fla. State. Hort., Soc., 112, 1-4.
- Carswell MC, Grant BR, Theodorou ME, Harris J, Niere JO, Plaxton WC 1996: The fungicide phosphonate disrupts the phosphate-starvation response in Brassica nigra seedlings. Plant Physiol., 110, 105-110.
- Carswell MC, Grant BR, Plaxton WC 1997: Disruption of the phosphate-starvation response of oilseed rape suspension cells by the fungicide phosphonate. Planta, 203, 67-74.
- Fenn ME, Coffey MD 1984: Antifungal activity of Fosetyl-Al and phosphorous acid. Phytopathology, 74, 606-611.
- Forster H, Adaskaveg JE, Kim DH, Stanghellini ME 1998: Effect of phosphite on tomato and pepper plants and on susceptibility of peppers to Phytophthora root and crown rot in hydroponic culture. Plant Dis., 82, 1165-1170.
- Grant, BR, Grant J, Harris J 1992: Inhibition of growth of phytophthora infestans by phosphate and phosphonate in defined media. Exp. Mycol., 16, 240-244.
- Guest D, Grant BR 1991: The complex action of phosphonates as antifungal agents. Biol Rev., 66, 159-187.
- Guest DL, Pegg KG, Whiley AW 1995: Control of Phytophthora diseases of tree crops using trunk-injected phosphonates. Horticultural Rev., 17, 299-330.
- Hsu HJ 1998: Inorganic phosphorous fertilizer. US Patent No. 5707418.
- Jackson TJ, Burgess T, Colquhoun I, Hardy GES 2000: Action of fungicide phosphite on Eucalyptus marginata inoculated with Phytophthora cinnamomi. Plant Path., 49, 147-154.
- Jee HJ, Cho WD, Kim CH 2002: Effect of potassium phosphonate on the control of phytophthora root rot of lettuce in hydroponics. Plant Pathol. J., 18(3), 142-146.

- Landschoot P, Cook J 2005: Sorting out the phosphonate products. GCM, 73, 73–77.
- Lee, TM, Tsai PF, Shya YT, Sheu F 2005: The effects of phosphite on phosphate starvation responses of *Ulva lactuca* (Ulvales, Chlorophyta). J. Phycol., 41, 975-982.
- Leymonie JP 2007: Phosphites and phosphates: When distributors and growers alike could get confused. Courtesy of New Ag International. Available from URL: http://www.spectrumanalytic.com/support/library/pdf/Phosphites\_and\_Phosphates\_When\_distributors\_and\_growers\_alike\_could\_get\_confused.pdf (accessed October 2008).
- Lovatt CJ 1990a: Foliar phosphorus fertilization of citrus by foliar application of phosphite. *In* Summary of Citrus Research. Ed. Citrus Research Advisory Committee, pp. 25-26. University of California, Riverside.
- Lovatt CJ 1990b: A definitive test to determine whether phosphite fertilization can replace phosphate fertilization to supply P in the metabolism of 'Hass' on 'Duke 7'. California Avocado Society Yearbook, 74, 61-64.
- Lovatt CJ 1996: Formulation of phosphorus fertilizer for plants. US Patent No. 5514200.
- Lovatt CJ 1998: Formulation of phosphorus fertilizer for plants. US Patent No. 5830255.
- Lovatt CJ 1999: Timing citrus and avocado foliar nutrient applications to increase fruit set and size. *HortTechnology*, 9 (4), 607–612.
- Lovatt CJ, Mikkelsen RL 2006: Phosphite fertilizers: What are they? Can you use them? What can they do? *Better Crops*, 90, 11-13.
- MacIntire WH, Winterberg SH, Hardin LJ, Sterges AJ, Clements LB 1950: Fertilizer evaluation of certain phosphorus, phosphorous and phosphoric materials by means of pot cultures. *Agron. J.*, 42, 543-549.
- McDonald AE, Grant BR, Plaxton WC 2001a: Phosphite (phosphorous acid): its relevance in the environment and agriculture, and influence on the plant phosphate starvation response. *J Plant Nutr.*, 24, 1505–1519.
- McDonald AE, Niere JO, Plaxton WC 2001b: Phosphite disrupts the acclimation of *Saccharomyces cerevisiae* to phosphate starvation. *Can. J. Microbiol.*, 47, 969–978.
- Mitchell C, Adam J 2004: Phosphite as fertilizer. Available from URL: http://www.aces.edu/timelyinfo/Ag%20Soil/2004/May/s-04-04-phosphite.pdf (accessed October 2008).

- Plaxton WC, Carswell MC 1999: Metabolic aspects of the phosphate starvation response in plants. *In* Plant Responses to Environmental Stresses, from Phytohormones to Genome Reorganization. Ed. HR Lerner, pp. 349–372. Marcel Dekker, New York.
- Rickard DA 2000: Review of phosphorus acid and its salts as fertilizer materials. J. Plant Nutr., 23, 161-180.
- Schroetter S, Angeles-Wedler D, Kreuzig R, Schnug E 2006: Effects of phosphite on phosphorus supply and growth of corn (Zea mays). Landbauforschu Volk., 3/4, 56, 87–99.
- Singh VK, Wood SM, Knowles VL, Plaxton WC 2003: Phosphite accelerates programmed cell death in phosphate starved oilseed rape (*Brassica napus*) suspension cell cultures. *Planta*, 218, 233–239.
- Smillie R, Grant BR, Guest D 1989: The mode of action of phosphite: Evidence for both direct and indirect modes of action on three *Phytophthora* sp. in plants. *Phytopathology*, 79, 921–926.
- Thao HTB, Yamakawa T 2008: Growth of celery (Apium graveolens var. dulce) as influenced by phosphite. Journal of the Faculty of Agriculture, Kyushu University, 53, 375-378.
- Thao HTB, Yamakawa T, Sarr PS, Myint AK 2008a: Effects of phosphite, a reduced form of phosphate, on the growth and phosphorus nutrition of spinach (Spinacia oleracea L.). Soil Sci. Plant Nutr., 54, 761–768.
- Thao HTB, Yamakawa T, Shibata K, Sarr PS, Myint AK 2008b: Growth response of komatsuna (*Brassica rapa* var. peruviridis) to root and foliar applications of phosphite. *Plant Soil*, 308, 1-10.
- Ticconi CA, Delatorre C A, Abel S 2001: Attenuation of phosphate starvation responses by phosphite in *Arabidopsis*. *Plant Physiol.*, 127, 963–972.
- Varadarajan DK, Karthikeyan AS, Matilda PD, Raghothama KG 2002: Phosphite, an analog of phosphate, suppresses the coordinated expression of genes under phosphate starvation. *Plant Physiol.*, 129, 1232–1240.
- Watanabe K 2005: A new fertilizer for foliar application, phosphite fertilizer. Fertilizer, 101, 91-96 (in Japanese).
- White AK, Metcalf WW 2007: Microbial metabolism of reduced phosphorus compounds. *Annu. Rev. Microbiol.*, 61, 379–400.
- Young DC 2004: Ammonium phosphate/phosphite fertilizer compound. US Patent No. 6824584.

9

\*





HG 42 2013

# Soil Amendments and Fertilizers Fertilizing Guidelines Included by Plant Group

Fertilizers and soil amendments are a wide array of materials added to soils to improve plant growth. They can be organic, such as bone meal, or inorganic, such as 10-10-10 fertilizer. Some must be purchased, while others are free for the taking from your landscape. Many are dual purpose—they serve as both fertilizers and soil amendments.

**Soil amendments** are anything mixed into topsoil to promote healthy plant growth. They function in a number of ways. For example, they may change the pH of soil or supply nutrients.

**Fertilizers** are primarily valued for their ability to supply nutrients. Plants use these nutrients to make components for plant growth such as proteins and carbohydrates.

One sub-set of soil amendments, **soil conditioners**, like composted horse manure, improve **soil structure** by binding soil particles into larger aggregates. This increases the amount of pore space and enhances air exchange, water movement, and root growth.

From the many "homegrown" and retail products available, the wise gardener selects those that most closely address a need while providing the best value for the money. Ask yourself if it makes sense to buy a fertilizer or amendment that hs traveled thousands of miles when local alternatives are available.

#### Feed The Soil First!

The surest way to improve plant growth is the regular incorporation of organic matter such as composted yard waste. Organic matter improves soil structure, slowly releases nutrients, and increases beneficial microbial activity.

#### **FERTILIZERS**

The main chemicals that must be supplied to plants are called **primary nutrients**. Those required in the greatest amounts

**Caution!!** Wear gloves and a dust mask when handling caustic or finely powdered materials. These include hydrated and burnt lime, perlite, vermiculite, and peat moss. Take similar precautions with bonemeal, fresh manure, and mulch.

are nitrogen (N), phosphorus (P), and potassium (K). Fertilizers are labeled with a three number analysis corresponding to N, P, and K. It tells what percentage of the net weight is actually composed of these three nutrients. A fertilizer containing all three nutrients is a **balanced fertilizer**. A 50-lb. bag of 10-6-4 fertilizer will contain 5 lb. of nitrogen (N), 3 lb. of phosphate ( $P_2O_5$ ), and 2 lb. of potash ( $K_2O$ ). (Phosphate and potash are the available forms of phosphorus and potassium respectively.) Some common N-P-K analyses of inorganic, granular fertilizers are 10-6-4, 5-10-5, and 10-10-10.

Plants also require the **secondary nutrients:** calcium, magnesium, and sulfur. Plus they need very small amounts of **micronutrients:** boron, copper, chlorine, iron, manganese, molybdenum, and zinc. These latter, plus a few others, are referred to as **trace elements**.

**Inorganic** or "chemical" fertilizers are typically less expensive (per pound of nutrient) and more readily available for plant growth than **organic fertilizers**. However, organic fertilizers often supply other nutrients in addition to N-P-K release nutrients slowly over the growing season, and may double as soil conditioners.

Words that appear in *italics* are trade names. Listed products are only examples and not endorsments.

Read All Product Label Instructions Before You Open the Bag!

\*Materials with an (\*) are considered acceptable by organic gardeners.

#### Contributions of primary nutrients to plant health:

- Nitrogen (N)- strong leaf growth, dark green color.
- Phosphorous (P)- roots, early plant growth, seed formation.
- Potassium (K)- plant vigor, disease and stress resistance, flavor and color enhancement.

Some fertilizers can be absorbed by plants immediately upon application. These are known as **quick release** or **highly soluble fertilizers**. They are useful when rapid results are required. They come in liquid or powder form and are applied to root zones or sprayed directly on foliage.

**Slow release fertilizers**, such as Osmocote and sulfur-coated urea, make nutrients available in small amounts over an extended period. Fertilizer stakes or tablets placed in root zone soil are also slow release formulations. However, salt accumulation resulting in root burn, can occur immediately adjacent to these latter products.

Fertilizers often target specific plant needs. For instance, **starter fertilizers** specially formulated for seedlings and transplants, are high in phosphorus to foster root establishment.

#### LIST OF FERTILIZERS

**Alfalfa meal\***: typically 3-5% organic nitrogen (3-1-2). May contain ethoxyquin, a preservative, to keep it green.

**Ammonium sulfate**: a dry fertilizer which is 21% N, plus sulfur. Very acidic, especially suitable for blueberries and azaleas, which require the ammonium form of nitrogen. Mix into soil to prevent loss of nitrogen to atmosphere.

**Blood meal\***: readily available nitrogen, typically 10-12%. Lasts about 2 months. May help repel deer and rabbits when top-dressed around plants.

**Bone meal\***: steamed ground bone high in phosphate. Sample analysis (1-11-0) or (5-12-0). Especially good for bulbs and root crops. Contains 15-22% calcium, plus trace elements. Lasts 6 to 12 months.

**Boron\***: micronutrient. Can be toxic to plants if applied in excess. Often applied by fruit growers to prevent fruit pitting and rot disorders. Deficiencies are most likely to occur on sandy soils. Incorporate 6-7 tablespoons of Borax per 1,000 sq. ft. of vegetable garden area each spring where soils are sandy.

Chelated iron\*: Chelated iron is applied to the folliage of

plants suffering from iron chlorosis (yellowing from iron deficiency.) Chelate means "claw" in Greek. Chelated elements are combined with compounds that hold them in solution, making them available for plant uptake through roots or leaves.

Compost tea\*: ordinarily homemade from "steeping" compost in a bucket of water (5 parts water to 1 part compost by volume) for 1-3 days, then straining and applying the brew to plants. Make compost tea using composted yard waste (leaves, grass clippings, etc.) or vermicompost (worm compost). Do not use farm animal manure compost. Good method for applying soluble nutrients directly to foliage or roots during the early part of the growing season when nutrients from soil organic matter are not readily available.

**Corn gluten\***: a natural pre-emergent herbicide. Apply in spring as a top-dressing to help control crabgrass and some weed species. It adds some organic matter and nutrients to the soil (10-1-1).

**Cottonseed meal\***: a slow release fertilizer high in nitrogen, that also adds organic matter (6-2-1). Lasts 6 months to 1 year.

**Epsom salts\***: magnesium sulfate, a highly soluble form of magnesium and sulfur. Can be used as a foliar spray for speedier results. Makes melons sweeter. Does not prevent blossom-end rot.

**Foliar fertilizers** are applied directly to the upper and lower leaf surfaces. Plants take up nutrients more efficiently through leaves than through roots. Foliar feeding is recommended to aid in the root growth and establishment of seedlings and transplants.

**Fish products\***: formulations range from fish powder (9-1-1), to fishmeal emulsion (5-1-1). Contain many valuable micronutrients. May have strong fishy smell.

**Greensand\***: a naturally occurring iron-potassium silicate (also called glauconite) with the ability to absorb 10 times more moisture than ordinary sand. It contains marine potash, silica, iron, magnesium, and lime, plus up to 30 other trace minerals. Dual ability to bind sandy soils and loosen clay soils. Potassium (5-7 %) released very slowly over 4 to 5 years. Slightly acidic.

**Guano\***: decomposed manure, usually of bat or seabird origin, was the first commercial fertilizer sold in the U.S. Desert bat guano escapes leaching in caves, preserving its nutrients. Seabird guano recycles marine trace elements. Valued for fast release and high N analysis (10-3-1). Suggested use is as a potting soil additive.

*Holly-Tone*, *Bulb-Tone*, etc.: mixtures of organics (animal tankage, crabmeal, kelp, and greensand) and inorganics (sulfate of potash, ammonium sulfate) that target specific plant groups. All contain 11-12 micronutrients.

Mix granular fertilizers into the top 4-6 inches of soil, then water the area well.

**Humates\***: a mined ancient organic soil. Unlike peat, humates are thoroughly decayed or mineralized, so nutrients are available to plants. Contains up to 35% humic acids that dissolve other nutrients for plant utilization. Manures and yard waste compost also contain humic acids.

**Kelp products\***: made from seaweed; contain dissolved ocean minerals. Dried kelp will usually contain 1.6 to 3.3% nitrogen, 1 to 2 % P<sub>2</sub>0<sub>5</sub> and 15% to 20% K<sub>2</sub>0. Also valued as a growth stimulant because of rich concentrations of trace minerals (over 60), amino acids, vitamins, and growth hormones, including cytokinins, auxins and gibberellins. Available in meal, powder, and liquid forms. Very good for seedlings and transplants.

**Manure**: (purchased) these products carry an NPK fertilizer analysis on their label and will also improve soil structure.

- Cow or Steer (dehydrated)\*— manure exposed to 180°F, dried to 17% moisture, and ground into a fine, soil-like texture. Nutrients are more concentrated and the soluble salt level is probably higher in dehydrated manure than in locally available farm manure.
- Cockadoodle Doo\*— (4-2-2) layer hen manure that has been dehydrated.
- Cricket\*— manure of crickets raised for bait (4-3-2).
   Because high salts may burn roots, add sparingly to potted plants.

*Milorganite*. A composted sewer sludge that has been heat dried and therefore has a higher N-P-K (5-2-5). Labeled for use in vegetable gardens in Maryland. Anecdotal evidence suggests composted sewer sludge repels rabbits, deer, voles, and squirrels when used as a top-dressing.

*Miracid*: high-solubility fertilizer (30-10-10) with chelated iron to combat chlorosis in acid-loving plants. Over-use may drop the pH too low.

*Miracle-Gro*: highly soluble fertilizer. Dissolve in water. Used as a foliar spray or applied directly to soil. Ammonium phosphate and urea sources of N. Contains six important icronutrients.

*Osmocote*: resin coated, slow release fertilizer (up to 4 month release outdoors). Many different analyses are available. Popular in the nursery and greenhouse industries.

**Rock products**: a wide variety. Be aware that the touted "immediately available" nutrients may refer to only a small percentage of the whole, while the rest will be released slowly. Not considered organic if treated with a chemical to increase nutrient solubility. A selection of those available follows:

- Azomite or rock dust\*— an aluminum silicate clay mixed with over 50 minerals, from marine deposits (2.5% potassium).
- Black rock phosphate\*— about 30% phosphate rock with calcium oxide, silicas, and trace minerals. Only 3% of phosphate immediately available. Slow release builds longer reserve than colloidal phosphate. Best in slightly acid soils.
- Soft rock or colloidal phosphate\*— phosphate clay with 18-22% phosphate, 27% calcium oxide, silicas, and 14 trace minerals. 2% phosphate immediately available, the rest slow-release over 3-5 years. Half the liming value of ground lime.
- Superphosphate (0-20-0) and triple superphosphate (0-45-0)—Phosphate rock treated with acid to make the phosphorus more soluble.

Seaweed products: See: "Kelp products"

**Soybean meal**: Similar to alfalfa and cottonseed meal with an analysis of 7-2-1. Can inhibit the germination of seeds planted right before or after an application.

*Sul-Po-Mag\**: sulfate of potash magnesia from the mineral langbeinite, with about 22% sulfur, 22% potash, and 18% magnesium oxide. Readily soluble.

**Stop Rot\***: a liquid formulation of calcium carbonate (CaCO<sub>2</sub>) used to prevent blossom-end rot in vegetable crops. Plants take up foliar sprays very efficiently.

Blossom-end rot of tomatoes is caused by a lack of calcium in the developing fruit. Prevent it by adding a small handful of finely ground limestone to each planting hole prior to transplanting. Water plants regularly and deeply and keep them mulched. Be aware that excessive nitrogen levels may block calcium uptake.

**Urea**: rapid nitrogen release (46-0-0) with a high "burn potential". Handle and use with care. Must mix into soil to prevent conversion to ammonia and subsequent escape into the air. **Sulfur-coated urea** is a slow release formulation.

**Wood ashes\***: analyses run from 1 to 2% phosphorus and from 4 to 10% potassium. Hardwood ashes are 45% carbonate equivalent and are half as effective as lime for raising soil pH. Softwood ashes are less effective than hardwood. Ashes are too fine to improve soil structure. The recommended yearly application rate is 25-50 lbs./1,000 sq. ft. At higher rates, test soil pH yearly.

Worm castings\*: the rich digested "soil" produced by redworm farming. No guaranteed listed analysis due to the great variability in feedstock, storage, and handling. Concentrated source of Ca, Mg, N, P and K, in readily available form. Used for container plants, indoors and out. Use 1 to 2 cubic feet per 100 square feet of garden area. Castings can be purchased through catalogs or produced at home in redworm bins.

#### SOIL CONDITIONERS

Most garden and landscape plants perform best in soils high in organic matter (greater than 2% organic matter, by weight, in the topsoil). These soils are loose, easy to work, and have a large number of earthworms. Organic matter is continuously used up through oxidation, downward movement through the soil profile, and plant growth. It should be replenished each year in cultivated flower and vegetable beds.

#### Coverage

3 cubic feet of organic matter will cover 36 sq. ft. to a depth of 1 inch.

Useful conversions: 7.5 gallons = 1 cu. ft.

1 cu. ft. = 1.25 bushels 27 cu. ft. = 1 cu. yd.

**Compost (commercial or "home-grown"):** made from decayed organic materials such as straw, corn cobs, food wastes, cocoa bean hulls, poultry litter, grass clippings, leaves, manure. Composts improve soil structure and slowly release nutrients to plant roots. (*See HG 35 Backyard Composting*)

**Gypsum\***: calcium sulfate, a mined product also called "land plaster." About 20-23% calcium and 15-18% sulfur, two secondary nutrients usually fairly well supplied in Maryland soils. The calcium is fast-acting. Also recommended to tie-up excess magnesium. Will leach sodium from soils with high salt concentrations caused by de-icing materials or ocean spray. Gypsum will not raise or lower soil pH.

**Humus\***: the stable, end product of the decomposition of soil organic matter. It holds water and nutrients, aids soil aggregation, is a source of humic acid and chelates, and contains huge microbial populations. May be purchased.

**Humic acid\***: an important component of organic matter. It's a very mild acid released in the decay process. Dissolves soil minerals, especially phosphorus, for plant use.

**LeafGro\***: composted leaves and yard debris from central Maryland. Approximate analysis 1-.5-1, with a pH range of 6.8-7.2. Holds 225% of its weight in water and does not repel water when dry as peat moss does. Use as a soil amendment, mulch, potting mix component, or top-dressing when seeding turf. Good peat moss substitute.

#### Use Manures Wisely

Apply uncomposted manure in the Fall only. Mix into the top 4-6 inches of your soil; don't leave it on top of the ground. Never use pet manure in the vegetable garden. Fully composted manure can be mixed into garden soil in Spring.

Manure (local)\*: sheep, cattle, horse, and chicken manure widely available from nearby farms. Ask for manure that has been mixed with bedding material and allowed to compost and age for at least 4-6 months. Farm manures usually contain 1% or less each of N, P, and K. Rabbit, sheep and chicken manure are higher in these nutrients. Manure mixed with urine-soaked bedding will be higher in N. Approximately 20-40% of the nitrogen is available to plants the first year after application. Weed problems may occur when the entire compost pile does not reach sufficiently high temperatures. A heavy organic mulch will help smother weeds.

**Mushroom compost\***: used or "spent" compost from mushroom farming. It is some combination of manures, wheat straw, corn cobs, feathermeal, peanut meal, peat moss, lime, etc. Mushrooms grown in this media use only a small portion of the many nutrients. Nutrient analysis: 2.75-1.5-1.5. Can have high soluble salt levels and should be fully incorporated and watered prior to planting.

**Peat moss\***: partially composted moss mined from prehistoric non-renewable bogs. Light and porous, it absorbs 10-20 times its weight in water. Its high surface tension causes it to repel water when it's dry, so do not use as mulch or top-dressing. Contains little nutrient value, but has a high nutrient-holding capacity. Acidic (as low as 3.0 pH); good for working into azalea and blueberry beds.

**Pine bark fines\***: a finely shredded pine bark product that retains moisture. Sometimes a composted component of potting media. May be incorporated into annual and perennial beds. Very acidic, so watch soil pH levels if large quantities are used. A peat moss alternative.

**Sand\***: to improve water drainage and aeration of clay soils a minimum of 50% by volume is necessary. Use only coarse builder's sand, not play sand. Often impractical to use because of the large volume needed.

**Sawdust\***: only well-decayed sawdust should be incorporated into the soil. Fresh sawdust can burn plant roots and "tie up" nitrogen as it decomposes. (Soil microbes that break down the high-carbon sawdust need nitrogen.) Good for mulching blueberry beds.

**Topsoil\***: no state or federal standards. Quality will vary. Inspect topsoil and ask for references. Inquire where it came from and whether any testing for pH, soluble salts, heavy

metals, etc. has been done. Avoid sticky, grayish, mottled, or foul-smelling soils.

Blended topsoil (70%) and leaf compost (30%) mixes are excellent for an instant raised bed garden. Can be purchased by the cubic yard.

Water-absorbing polymers: super-absorbent polymer granules that can absorb 300-400 times their weight in water. As soil dries, stored water is released slowly back into soil. Also absorbs and releases fertilizer. The cost-effectiveness of these materials has not been demonstrated for outdoor garden use.

#### **GROWTH STIMULANTS**

See also: Humus, Kelp products

**Bioactivators\***: various commercial products containing one or more of the following: beneficial bacteria, growth hormones and stimulants, nutrients, and vitamins. May be useful as a "tonic" for the lawn, seedlings, transplants, and plants languishing in cool soils in the spring. These are unnecessary for backyard compost piles.

*Microp\**: soil innoculant. When sprayed on the soil these nitrogen-fixing algae grow rapidly and can supply 30 to 60 lbs. of nitrogen per acre, plus producing polysaccharides (the soil aggregating compounds in humus) which combat soil compaction.

**Mycorrhizae\***: Are beneficial fungi which grow symbiotically on or in roots and extend the root structure by sending out tiny filaments to forage for nutrients. Some crops, like blueberry, rely heavily on mycorrhizae for nutrient uptake.

**Nitrogen-fixing bacteria innoculant\***: a powder used to coat legume (pea, bean, and clover) seed to increase the growth of nitrogen-fixing nodules on their future roots.

#### pH ADJUSTORS

See also: Ammonium sulfate, Gypsum, Miracid, Shellfish products, and Wood ashes

**Aluminum sulfate\***: *not* recommended as a soil acidifier because it can cause a toxic aluminum build-up (Maryland soils have adequate aluminum levels). Iron sulfate and elemental sulfur are preferred.

**Iron sulfate\***: lowers pH. Turns hydrangea flowers blue. It contains 20% iron. Use 3-4 times the recommended amount of "plain" elemental sulfur. (In a medium texture soil, lower the pH by ½ unit by applying 12-14 lbs./1000 sq. ft. of area.) See: *Sulfur* 

**Lime\***: raises pH. There are several kinds of naturally occurring mined limestone:

- **Aragonite\*** or oyster shell lime, is 96% calcium carbonate mined off the coast of Bermuda. Less quickly available than ground ag lime, but it lasts 4-5 years.
- Agricultural limestone\* "Ag lime"- a finely granulated calcitic limestone. The finer the grind or mesh size, the more readily it will act to raise soil pH. Powdered lime is faster acting.
- **Hydrated lime\*** calcium hydroxide, produced by adding water to burnt lime. Quick acting. Need apply only 75% of calcitic recommendation.
- **Burnt lime\*** calcium oxide, very caustic. (Also known as "quick lime".) Produced by heating limestone to a very high temperature. Apply only 50% of calcitic recommendation. Will burn plant roots upon direct contact.
- Dolomitic lime\*- contains calcium carbonate and magnesium carbonate. Recommended for raising pH on low magnesium soils.
- Pelletized lime\*- very similar to ground ag lime, but easier to apply in this pellet form.
- Wood Ash See page 3

**Sulfur\***: elemental sulfur, sold as "flowers of sulfur" or micro-fine sulfur, is used to lower soil pH. At pH above 6.0, iron sulfate lowers pH more quickly than sulfur.

#### Soil pH

Soil pH is a measure of the hydrogen ion concentration of soil. A pH value of 7.0 is neutral. Readings below 7.0 are acidic and those above 7.0 are alkaline. Soil nutrients are most available to plant roots and microbial activity is greatest when soil pH is in the 5.5 to 7.0 range. Plants may show symptoms of nutrient deficiency or toxicity at very high or low soil pH. For example, azaleas grown in high pH soil may have yellow leaves due to a deficiency of iron (iron chlorosis). Liming is best accomplished in the fall, because lime requires time to change pH.

#### POTTING MIXES

See also: Peat moss

**Perlite\***: a very lightweight heat-expanded volcanic mineral which provides drainage and oxygen space in soils. Does not hold nutrients or water but is especially effective for increasing the porosity of potting media.

**Potting soil\***: a generic term used to describe products that vary widely in composition, weight, and nutrient content. Some are dense and not good for growing seedlings.

Soilless mix\*: a sterile mix of peat moss, perlite and vermiculite. May also contain coir, compost, bark, and chips and other ingredients. Recommended for growing seedlings. Also fine for indoor and outdoor container gardening. Soilless mixes, like *Pro-Mix*, *Reddi Earth*, and *Sunshine Mix*, have a small amount of added fertilizer, so they can sustain a crop of flower and vegetable seedlings for 4-6 weeks without the need for additional fertilizer. Work water into these mixes by hand prior to use.

**Vermiculite\***: mica-type mineral heated in high temperature furnaces to form sterile, expanded, fan-like particles with many air spaces which promote aeration and water movement. Absorbs and holds nutrients and water (unlike perlite). Also rich in trace elements.

#### FERTILIZER GUIDELINES BY PLANT GROUP

Good health in plants depends on a continuous supply of available nutrients from the soil or, in the case of container plants, the growing media. Nutrient needs vary from plant to plant and the ability of the soil to supply those nutrients varies from site to site.

Take a soil test of major areas of your landscape — front and back lawn, vegetable garden, large flower beds — every 3-4 years to determine nutrient levels. (See HG 110 Selecting and Using a Soil Testing Laboratory.) Nutrients levels are often in the "excessive" range in older and well-tended landscapes. This is not a problem for plants. It simply means you don't need to add these nutrients for some time.

Most garden and landscape plants grow best in a soil pH range of 6.0-7.0. Many nutrients become either unavailable or overly-abundant outside this range. Pay close attention to your soil pH readings and be prepared to adjust them according to your soil test recommendations.

Fertilizers won't necessarily help sick plants, if the cause of poor growth is related to insect, disease or environmental problems and not to a lack of nutrients. Overuse of fertilizers can lead to weak, succulent growth, encourage insect pests and disease problems, and contribute to water pollution.

#### 10 Ways to Conserve Nutrients, Prevent Pollution, and Improve Soil

- Take a soil test every 3 to 4 years. Fertilize according to soil test recommendations. For lawns, follow University of Maryland Extension recommentations. Do not exceed label directions.
- 2. Keep fertilizers off hard surfaces. Rain water will carry fertilizer salts into storm drains and surface waters and contribute to nutrient pollution of our waterways.
- Keep bare soil covered with a mulch or plant a cover crop or ground cover. Over time, rainfall causes bare soil to erode and become compacted. Grow ground covers in place of turf in deep shade.
- 4. Leave grass clippings on your lawn (grasscycling.)
  They are a source of nitrogen for your lawn and will not contribute to thatch build-up in fescue or bluegrass lawns.
- 5. Keep stored manures and compost covered to prevent leaching of nutrients.
- 6. Incorporate or compost plant residues. However, discard

- plants with serious disease problems.
- When appropriate, substitute slow-release fertilizers for those that are highly soluble and substitute locally available organic fertilizers like farmyard manure, backyard compost, and municipal leaf compost for manufactured chemical fertilizers.
- 8. Avoid excessive foot or equipment traffic to prevent soil compaction, especially when the soil is wet.
- 9. Avoid cultivating soils on steep slopes. Construct terraces where appropriate.
- 10. To melt winter ice, use calcium magnesium acetate (CMA), potassium chloride (KCl), or calcium chloride (CaCl<sub>2</sub>). Do not use sodium chloride, urea, potassium nitrate, or other chemical fertilizers containing nitrogen or phosphorous. The salts in these fertilizers may burn the foliage and roots of adjacent plants and wash into and pollute waterways. (See FS 707 Melting Ice Safely)

Home gardeners tend to over-fertilize flower and vegetable beds. Plan to reduce or eliminate fertilizer applications in these areas if an inch or more of organic matter is incorporated into the soil of established beds at least once a year.

Use the information below as a starting point for planning how to fertilize your plants. In all cases, organic fertilizers (e.g. soybean meal) can be substituted for inorganic fertilizers (e.g. 10-6-4).

#### Trees:

- Healthy, mature trees do not usually benefit from fertilization. Trees in the landscape receive nutrients from turf fertilization, grass clippings, fallen leaves and natural soil fertility.
- Tree spikes are not recommended.

#### Shrubs:

- Shrubs that are surrounded by fertilized turf receive adequate nutrients and don't require additional fertilizer. The breakdown of organic mulches also contributes nutrients.
- Where growth is lagging, top-dress shrub beds with well-decomposed compost or apply a balanced fertilizer (e.g. 5-10-5, 10-6-4) in the late fall or early spring at the rate of 1 lb. per 100 sq. ft. of area.

#### Annual flowers:

- No fertilizer may be necessary if beds are heavily amended with organic matter. However, flower size and overall production can be increased with supplemental fertilization.
- In new gardens low in organic matter, apply 2-4 lbs. of 5-10-10 per 100 sq. ft. of area or other comparable fertilizer. Incorporate fertilizer into the top 6 inches of soil in early spring before planting.

Sweep or wash granular fertilizers off foliage to prevent leaf burn.

#### Herbaceous perennials:

- No fertilizer may be necessary if beds are heavily amended with organic matter.
- In new gardens low in organic matter, apply 2-4 lbs. of 5-10-10 per 100 sq. ft. of area or other comparable fertilizer. Broadcast the fertilizer lightly around plants in early spring.

#### Vegetables:

 No fertilizer may be necessary if beds are heavily amended with organic matter.

- In new gardens low in organic matter, apply 2-4 lbs.
   of 5-10-10 per 100 sq. ft. of area. Fertilizer should be
   applied and incorporated into the top 6 inches of soil in
   early spring.
- Early season crops benefit from quick-acting foliar or liquid fertilizers, or compost tea.
- Perennial crops, like asparagus and rhubarb, are fertilized in early spring and after harvest.

#### Fruit:

- Most fruit plants are fertilized at flowering. Junebearing strawberries are fertilized in July after harvest.
- Peaches require annual applications of fertilizer. Apple and pear trees should not be fertilized if the trees are healthy and productive (making 18-24 inches of new shoot growth each year.)
- Blueberry plants require a soil pH in the 4.5-5.0 range and should be fertilized each spring after bloom with ammonium sulfate.

#### Houseplants:

- Fertilize with a commercial fertilizer containing micronutrients or add a small amount of wellcomposted, screened leaf mold or other compost each year. Compst tea is also commonly used.
- Because magnesium leaches from the soil at each watering, replace it with a solution of 1 teaspoon Epsom salts per gallon of water. Water with this solution two times each year or use the solution as a leaf spray.
- During the winter months, houseplants don't need fertilizer because reduced light and temperature result in reduced growth. Fertilizing at this time could harm some plants, unless they are actively growing.
- Monthly applications of a dilute liquid fertilizer in the summer months will keep most plants healthy.
- Excessive fertilizer results in the buildup of salts (as
  evidenced by a white coating on the inside of pots)
  leafburn, and excessive, leggy growth. Flush out
  excessive salts by pouring a large amount of water
  through the growing media.

#### Herbs:

 Apply fertilizers sparingly. Many herbs, especially the "Mediterranean" herbs, such as basil, thyme, rosemary, oregano and lavender, grow best on sunny, dry sites in light (sandy) soil. Heavy applications of fertilizers or organic matter may lower the plant's essential oil content and encourage root and stem rot diseases.

Turf: See HGIC website for current recommendations

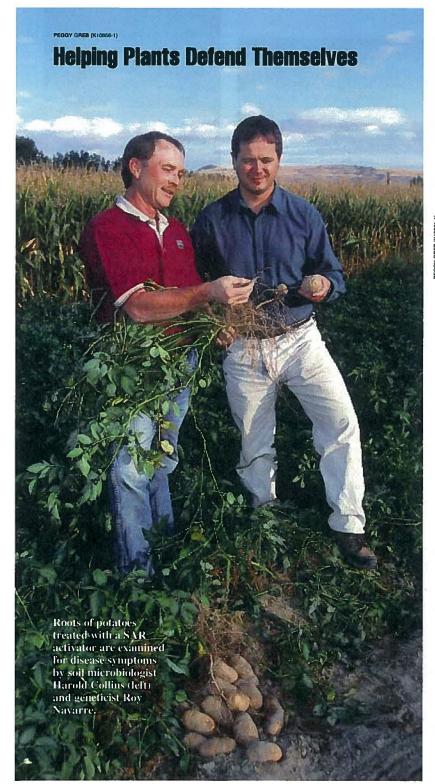
Mention of specific commercial products and trade names does not constitute an endorsement by the University of Maryland.

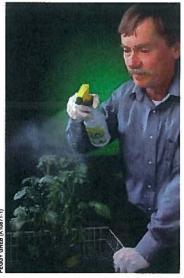
# Do you have a plant or insect pest question? Visit us at extension.umd.edu/hgic and click Ask Maryland's Garden Experts

Authors: Jon Traunfeld, University of Maryland Extension Specialist, and Ellen Nibali, Horticulture Consultant, University of Maryland Extension, Home and Garden Information Center

This publication is a series of publications of the University of Maryland Extension and The Home and Garden Information Center. For more information on related publications and programs, http://extension.umd.edu/hgic. Please visit http://extension.umd.edu/ to find out more about Extension programs in Maryland.

The University of Maryland, College of Agriculture and Natural Resources programs are open to all and will not discriminate against anyone because of race, age, sex, color, sexual orientation, physical or mental disability, religion, ancestry, or national origin, marital status, genetic information, or political affiliation, or gender identity and expression.





Peter Landolt, head of ARS's Fruit and Vegetable Insect Research Unit, Wapato, Washington, applies a plant hormone precursor to a potato plant to induce chemical defenses against insects.

eople aren't the only ones to benefit from salicylic acid, the active ingredient in aspirin. Research has shown that spraying this naturally occurring compound onto some plants triggers natural defenses that keep harmful fungi, bacteria, and viruses at bay.

Plants have always had some means to defend themselves; it's just that some don't recognize their microbial attackers in time. Spraying salicylic acid or certain other compounds snaps them to attention and puts their defenses on highalert against future attacks.

Plant scientists first encountered the phenomenon, called systemic acquired resistance (SAR), in the 1930s. Plants make salicylic acid, particularly after encountering a pathogen, and use it as a key regulator of SAR and expression of defense genes. But only recently have companies begun marketing salicylic acid and other similar compounds as a way to activate SAR in crops—tomato, spinach, lettuce, and tobacco among them.

Little is known about the benefits of such products on potatoes, but a team of Agricultural Research Service (ARS) scientists in Prosser, Washington, has begun studies to find out.



ARS scientists are experimenting with spraying natural compounds on potato plants to induce plant resistance to fungal and insect pests like these cabbage looper larvae, shown here on potato leaves.



Technician David Mayo prepares to extract RNA from samples of potato leaves treated with a SAR activator.

"A major objective of our research is to understand how SAR functions in potatoes so that we can ultimately use it in the field for disease control," says Roy Navarre, a molecular biologist and team leader at ARS's Vegetable and Forage Crops Research Unit in Prosser. "Systemic acquired resistance is a basic mechanism by which plants protect themselves, so we want to take advantage of that as much as possible."

Navarre's chief collaborators are ARS scientists Pete Thomas, Chuck Brown,

Nik Grunwald, Hal Collins, and Peter Landolt. Pradeep Kachroo, another collaborator, is with the University of Kentucky-Lexington. The Washington State Potato Commission partly funded the project.

If spraying salicylic acid or other compounds on potatoes to activate SAR works, it should help ease reliance on synthetic pesticides to battle various disease organisms and insects that can diminish the tuber yields and quality of potatoes, a crop that generates nearly \$3 billion annually in U.S. farm sales and is a staple food for 1.5 billion people worldwide.

#### **Rousing Dormant Defenses**

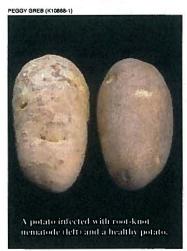
Particularly intriguing is the prospect of activating SAR as a fast, cost-effective means of protecting cultivars that are agronomically profitable but prone to disease.

> "Plants may have all the tools they need to be resistant to certain pathogens. It's just that sometimes they become infected because they don't turn on their defenses rapidly enough," says Navarre. "If we can get SAR to flip this switch, we could extend the life and usefulness of susceptible but otherwise good cultivars."

In nature, SAR can begin when a single fungal spore lands on a leaf and germinates there. Plants can have what's called a hypersensitive response. It commands cells at the site of infection to kill themselves, which helps cordon off the microbial invader. About a week later, a signal travels from the site of infection on the leaf to the rest of the plant, activating a battery of defense mechanisms. Plants then synthesize antimicrobial substances, including the protein chitinase, which degrades the cell walls of fungi, and enzymes called nucleases, which break apart the ribonucleic acid of viruses.

Despite extensive research on SAR in model plant systems like *Arabidopsis* and tobacco, Navarre says much has still to be learned about the defenses that signal compounds like salicylic acid to activate in potatoes.

In earlier studies, for example, he and co-investigators showed that the leaves and roots of potato plants naturally contain 100 times more salicylic acid than many other crops. Perhaps as a result, some of the defense genes involved in SAR are usually active to some degree—even if no infection has occurred.



#### **Pest-Proofing Potatoes**

The pathogens the researchers hope to stymie by activating SAR or similar defenses include fungi that cause the diseases late blight, white mold, and early dying complex, as well as two nonmicrobial pests. One pest is the green peach aphid, a soft-bodied, sap-sucking insect that spreads 10 different potato viruses. The other is the Columbia root-knot nematode. In the Pacific Northwest, where much of the U.S. potato crop is grown, farmers often spend \$250 an acre chemically fumigating their fields to get rid of the nematode before planting time. But one such fumigant, methyl bromide, is scheduled for complete phaseout by 2005 because of environmental concerns.

Earlier this year, Navarre's team began greenhouse experiments to monitor the effectiveness of salicylic acid and other activators in helping potato plants resist viruses, including potato virus Y.

"Potato viruses are the first pathogens we chose to work on because they're such a threat to the potato crop," says Navarre. "Furthermore, there aren't many economically feasible products that directly inhibit plant viruses, whereas SAR can be effective." But the activators the researchers are using don't act directly on the pathogens. Instead, their role is to stimulate plants' defense responses to attack.

For this study, the researchers first grow miniature potato plants from tissue culture. This ensures that the plantlets used in the study are free of pathogens that can trigger SAR activity before it's desired. The scientists then spray two groups of about 50 plantlets with the activators. A third group is left alone as a control. After that, they inoculate the plants with the virus, later checking them for disease symptoms, such as a yellowing of the leaf. They also check for the virus in tissue specimens taken from the plants, using ELISA (enzymelinked immunosorbent assay) and PCR (polymerase chain reaction) tests.

Though the studies are still ongoing,

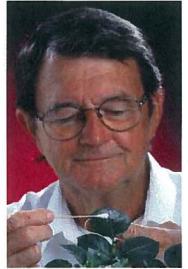


Roy Navarre extracts salicylic acid from potato leaves and measures it with high-performance liquid chromatography.

"preliminary results are encouraging that SAR can be an effective potato defense," Navarre reports. Similar studies are planned later this year for other pathogens and the Columbia root-knot nematode.

Meanwhile, at ARS's Fruit and Vegetable Insect Research Unit in Wapato, Washington, research leader Peter Landolt is activating the potato plants with plant hormones to identify specific defense chemicals that stymie feeding by aphids and leaf-eating caterpillars such as the alfalfa looper. "We're trying to

PEGGY GREB (K10862-1)



A potato leaf previously treated with a SAR activator is inoculated with potato virus Y by virologist Pete Thomas.

figure out which of these chemicals the potato plant strengthens as a way to defend itself against attack by these insects," says Landolt.

Another research component involves measuring the degree to which SAR is expressed in treated plants, as well as in the plants' leaves, stems, roots, and tubers. The researchers are also spraying the plants with different application rates to find the best doses to use.

"It's possible one activator may be more effective in leaves and a different one more effective in the roots," Navarre explains. "So, if one is looking for resistance to a root pathogen, it's important to be using the compound and dosage that work best in roots."

On yet another front, his team is monitoring how long it takes for SAR to kick in once the plants have been sprayed and how long it is effective. In a crop field, such information would "influence how often plants need to be treated," Navarre says. Studies in tobacco and other crops show that SAR can last for weeks to months. What's more, the plant during this period can resist pathogens other than the one that originally triggered the response.

Another interest is to identify and clone plant defense genes that are involved in boosting the effect of salicylic acid. Such genes could then be used by potato breeders to make new potato cultivars that can better resist diseases. Until then, "The better we're able to understand SAR, the better we'll be able to use it," says Navarre.—By Jan Suszkiw, ARS.

This research is part of Plant Molecular and Biological Processes, an ARS National Program (#302) described on the World Wide Web at www.nps.ars. usda.gov.

To reach scientists featured in this article, contact Jan Suszkiw, USDA-ARS Information Staff, 5601 Sunnyside Ave., Beltsville, MD 20705-5129; phone (301) 504-1630, fax (301) 504-1641, e-mail jsuszkiw@ars.usda.gov. ★



# BIOPESTICIDES REGISTRATION ACTION DOCUMENT

Complex Polymeric Polyhydroxy Acids (CPPA)
PC Code: 078503

U.S. Environmental Protection Agency Office of Pesticide Programs Biopesticides and Pollution Prevention Division

# 

# TABLE OF CONTENTS

I.	EXECUTIVE SUMMARY	4
II.	ACTIVE INGREDIENT OVERVIEW	6
III.	REGULATORY BACKGROUND	
	B. FOOD CLEARANCES/TOLERANCES	
IV.	RISK ASSESSMENT	7
	A. ACTIVE INGREDIENT CHARACTERIZATION  B. HUMAN HEALTH ASSESSMENT	
	C. ENVIRONMENTAL ASSESSMENT	11
	D. EFFICACY DATA	12
v.	RISK MANAGEMENT DECISION	13
	A. DETERMINATION OF ELIGIBILITY FOR REGISTRATION	13
	B. REGULATORY DECISION	13
	C. ENVIRONMENTAL JUSTICE	14
VI.	ACTIONS REQUIRED BY REGISTRANTS	14
	A. REPORTING OF ADVERSE EFFECTS	14
	B. REPORTING OF HYPERSENSITIVITY INCIDENTS	14
VII.	APPENDIX A. DATA REQUIREMENTS (40 CFR PART 158-SUBPART U)	14
VIII.	APPENDIX B	21
IX.	APPENDIX C	21
v	CLOSSADY OF ACRONYMS AND ARREFULATIONS	24

# **BIOPESTICIDES REGISTRATION ACTION DOCUMENT (BRAD) TEAM**

Branch Chief Linda A. Hollis, M.S.

Product Chemistry/Human Health Effects/Nontarget Organisms Russell Jones, Ph.D, Senior Scientist

Regulatory Action Leader Menyon Adams, Biologist

#### I. EXECUTIVE SUMMARY

The active ingredient subject to registration, Complex Polymeric Polyhydroxy Acids (CPPA), is derived from naturally occurring organic matter (NOM) in soils and ground and surface waters. NOM is ubiquitous in soil and water. It is formed as a result of the decomposition of plants, animal, and microbial materials in soil and water, and is comprised of a variety of humic substances such as tannins, humic acids and fulvic acids. CPPA contains a complex mixture of these naturally occurring organic substances and has been adequately characterized by the applicant. CPPA is obtained by collecting water that has leached through forest soil and concentrating the desired substances (humic acids, fulvic acids and tannins) via a proprietary manufacturing process.

The Biopesticides and Pollution Prevention Division (BPPD) determined that the guideline studies submitted for product chemistry Technical Grade Active Ingredient (TGAI)/Manufacturing-Use Product (MP) and End Use Product (EP) data requirements and Tier I acute toxicity (EP) data requirements for CPPA satisfy the current data requirements. BPPD also determined that the acceptable non guideline studies and technical journal articles from the open literature that were submitted in lieu of studies for the Tier I toxicity data requirements for CPPA TGAI/MP, satisfy the current data requirements.

For nontarget organisms and environmental fate data requirements (OCSPP 850.1010 to 850.4450) guideline studies, technical journal articles (in lieu of studies) from the open literature and waiver requests were all submitted to support non-target birds, non target fish, non target aquatic organisms, and non-target aquatic plants data requirements. An acute contact toxicity study with honey bees (*Apis mellifera*; *strain*: *Carniolan*) was also submitted in support of non-target organism data requirements.

Based on the acute toxicity data on the Technical Grade Active Ingredient (TGAI), CPPA is classified as toxicity category IV. Tier I subchronic oral toxicity, subchronic dermal toxicity, subchronic inhalation toxicity, and pre-natal developmental toxicity biochemical data requirements were satisfied with information from the open literature. Based on this information, CPPA demonstrates a lack of toxicity via these routes of exposure, and therefore will not have any subchronic toxicity effects, is not mutagenic, and is not genotoxic. The lack of toxicity is further supported by the low seasonal application rate (0.0064 lbs a.i./A), and the expected minimal residues in terrestrial (< 2 ppm) and aquatic (0.000355 ppm) environments, which are well below any definitive and non definitive toxicological endpoints identified in the scientific literature. EPA has concluded that it is in the best interests of the public to issue the registrations for the MP, Carbon Power Concentrate, and the EP, Carbon Power® (EPA File Symbol Nos. 84846-G and –E, which contain this new active ingredient, CPPA at 0.9% and 0.18%. respectively.

BPPD has reviewed the data/information in support of the requirements for granting registration under Section 3(c)(5) of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and has determined that the data/information submitted adequately satisfy current biochemical data requirements (please refer to 40 CFR § 158.2010).

On October 1, 2009, EPA announced a new policy to provide a more meaningful opportunity for the public to participate on major registration decisions before they occur. According to this policy, EPA provides a public comment period prior to making a registration decision for the following types of applications: new active ingredients, first food use, first outdoor use, first residential use; and any registration decisions for which the Agency believes there may be substantial public interest.

Consistent with the policy of making registration actions more transparent, CPPA is subject to a 15 day comment period as a "new active ingredient". The notice for this comment period includes the draft Biopesticides Registration Action Document (BRAD) and draft product labels for the MP, PROBLAD PLUS, which contains this new active ingredient, CPPA. The docket identification (ID) number is EPA-HQ-OPP-2009-0917. The Agency believes, based on the risk assessment and information submitted in support of the registrations of the MP and EP containing CPPA, it is in the best interest of the public to issue registrations for Carbon Power Concentrate, and Carbon Power®. The basis for this decision can be found in the risk assessments for CPPA, which is characterized in this BRAD.

to it test stockering with our men and the beautiful to our

# II. ACTIVE INGREDIENT OVERVIEW

Common Name: Complex Polymeric Polyhydroxy Acids

Chemical Names: N/A

Trade & Other Names: N/A

CAS Registry Number: N/A

OPP Chemical Code: 078503

Type of Pesticide: Biochemical Pesticide (Plant Growth Regulator)

# III. REGULATORY BACKGROUND

On October 31, 2009, EPA received applications, filed by Floratine Biosciences Inc., 153 N. Main St., Suite 100, Collierville, TN 38017, to register the products, Carbon Power Concentrate (EPA File Symbol No. 84846-G) and Carbon Power® (EPA File Symbol No. 84846-E), containing the new biochemical active ingredient, CPPA. A notice of receipt (NOR) of this application, allowing for a 30-day comment period, was published in the Federal Register on January 20, 2010 (75 FR 3235). One comment submitted by Salley O'Donnell, Lane County Audobon Society was received following this publication and is described below.

A comment was posted to the NOR docket ID number EPA-HQ-OPP-2009-0917 from Salley O'Donnell, Lane County Audobon Society on February 18, 2010. Mrs. O'Donnell believes it should be a requirement that all ingredients be disclosed on the pesticide product label since pesticides are commonly used where we live, shop, play, work and go to school. EPA thanks Mrs. O'Donnell for her comment regarding the NOR for Complex Polymeric Polyhydroxy Acids. The applicable Federal regulations governing pesticide labeling are found at (40 CFR § 156.10). The full composition of a product's formulation, by law, is considered confidential business information and therefore is not disclosed. The regulations specifically state that the label of each pesticide product must bear a statement that contains the name and percentage by weight of each active ingredient, the total percentage by weight of all inert ingredient; and if the pesticide contains arsenic in any form, a statement of the percentages of total and water-soluble arsenic calculated as elemental arsenic. The active ingredient(s) must be designated by the term "active ingredients" and the "inert ingredients" or the singular forms of these terms when appropriate. Further, both terms shall be in the same type size, be aligned to the same margin and be equally prominent. In the event that the product does not contain an inert ingredient, the term "inert ingredient" is not required. EPA may alternatively require the name of any inert ingredient(s) to be listed in the ingredient statement if it is believed that such ingredient(s), may pose a hazard to man of the environment however, EPA has not made that determination for this product.

#### A. Classification

On February 09, 2009, the Biochemical Classification Committee classified Humic Acids (Complex Polymeric Polyhydroxy Acids) as a biochemical active ingredient due to its nontoxic mode of action, natural occurrence in the environment, and history of exposure to animals and humans with minimal to nonexistent toxicity.

# B. Food Clearances/Tolerances

The applicant filed a petition (PP 9F7645) proposing to establish an exemption from the requirement of a tolerance for residues of Complex Polymeric Polyhydroxy Acids in or on all food commodities. A notice of filing (NOF), allowing for a 30-day comment period, was published in the Federal Register on January 13, 2010 (75 FR 1775). No comments were received following this publication.

# IV. RISK ASSESSMENT

# A. Active Ingredient Characterization

Complex Polymeric Polyhydroxy Acids are derived from naturally occurring organic matter [NOM (i.e., humic substances)] in soils and ground and surface waters. NOM is formed as a result of the decomposition of plant, animal, and microbial materials in soil and water (Anonymous, 2009), and is comprised of a variety of humic and non-humic substances (Sannigrahi, 2005).

CPPA is derived from the waters of a river receiving precipitation water that has percolated through Nordic forest soil located in Southern Sweden. The forest soil is described by the registrant as a "highly organic forest and marshland soil." The registrant further describes the area as a "low intensity managed conifer and mixed deciduous forest."

Descriptions of the product formulation and production process, formation of impurities, and physical and chemical characteristics were examined by BPPD and found to be acceptable in meeting current guideline standards.

NOM does not have a unique structure or composition, cannot be crystallized, and is extremely difficult to characterize (Anonymous, 2009). NOM is an undesirable component of drinking water due to organoleptic effects (UNESCO, 2010).

All product chemistry data requirements for registration of CPPA have been satisfied.

For more information regarding product chemistry data requirements, refer to Tables 1 and 2 in Appendix A.

# B. Human Health Assessment

## 1. Toxicology

For acute toxicity data requirements, toxicity categories are assigned based on the hazard(s) identified from studies and/or information on file with the Agency. The active ingredient is classified into Toxicity Category I, II, III or IV where Toxicity Category I indicates the highest toxicity and Toxicity Category IV indicates the lowest toxicity.

Adequate mammalian toxicology data/information is available to support the registration of CPPA. All toxicology data requirements for CPPA have been **satisfied**.

# a. Acute Toxicity

Acute toxicity testing is required to 1) determine systemic toxicity from acute exposure via the dermal, inhalation and oral routes, 2) determine irritant effects from exposure to the eyes, and 3) determine the potential for skin sensitization (allergic contact dermatitis).

The results from the Tier I acute toxicity testing on the manufacturing use product and information found in published literature supports the Agency's conclusion that CPPA is classified as a toxicity category IV compound via the acute dermal, oral, and inhalation routes of exposure, based on testing at a limit dose of 2000 mg a.i./kg in rats. There were no observable symptoms based on testing limits found in guinea pigs. And CPPA is not a dermal sensitizer.

For more information regarding acute toxicity data requirements, refer to Table 3 in Appendix A.

# b. Subchronic Toxicity

Subchronic data are required to determine a no-observed-effect-level (NOEL) and any toxic effects associated with repeated or continuous exposure to a test substance for a period of ninety days.

In lieu of data, a rationale for lack of repeated exposure to CPPA was submitted to address the subchronic [90-day dermal (OCSPP 870.3250) and 90-day inhalation (OCSPP 870.3465)] data requirements. BPPD determined that the rationale(s) submitted are acceptable based on the TGAI/MP toxicological and exposure profile, summarized in Table 4 in Appendix A.

In lieu of a guideline study conducted on the technical material, four studies from the open technical literature, and one data summary from the European Agency for the Evaluation of Medicinal Products (EMEA), were submitted to the Agency to support the data requirement (OCSPP 870.3100). The first two studies (Condie et. al., 1985; Daniel et. al., 1991) evaluated the subchronic toxicity of humic acids in unchlorinated and chlorinated drinking water in rats, and the third study evaluated the subchronic oral toxicity of gallic acid (a tannin) in rats (Niho et. al., 2001). In addition, a fourth study was submitted that evaluated the combined chronic toxicity

and carcinogenicity of unchlorinated and chlorinated humic acid in mice (Van Duuren et. al., 1986). The EMEA data summary was not used due to the lack of detail provided in the experimental methodology.

For more information regarding the subchronic data requirements, refer to Table 4 in Appendix A.

# c. Developmental Toxicity and Mutagenicity

In lieu of a guideline study conducted on the technical material, two studies from the open technical literature were submitted for the developmental toxicity data requirement (OCSPP 870.3700) and two studies from the open literature were submitted in support of the mutagenicity data requirement (OCSPP 870.5300 and 5375). BPPD determined the studies to be acceptable. As a result of the submitted data, tannic acid and humic acids (major CPPA components) are not mutagenic or genotoxic. The results also show humic acid to have NOEC levels of 125 ppm and 10 ppm, respectively.

For more information regarding developmental and mutagenicity data requirements, refer to Table 4 in Appendix A.

## d. Tier II/Tier III

Tier II and III data were not required due to the nature of the active ingredient and its intended uses as a plant growth regulator on field and greenhouse crops, fruits, nuts, vines, and ornamentals to improve germination and seedling development, stimulate root and shoot growth, increase chlorophyll content, improve stress resistance, and increase yields.

#### e. Effects on the Endocrine System

As required under FFDCA section 408(p), EPA has developed the Endocrine Disruptor Screening Program (EDSP) to determine whether certain substances (including pesticide active and other ingredients) may have an effect in humans or wildlife similar to an effect produced by a "naturally occurring estrogen, or other such endocrine effects as the Administrator may designate." The EDSP employs a two-tiered approach to making the statutorily required determinations. Tier 1 consists of a battery of 11 screening assays to identify the potential of a chemical substance to interact with the estrogen, androgen, or thyroid (E, A, or T) hormonal systems. Chemicals that go through Tier 1 screening and are found to have the potential to interact with E, A, or T hormonal systems will proceed to the next stage of the EDSP where EPA will determine which, if any, of the Tier 2 tests are necessary based on the available data. Tier 2 testing is designed to identify any adverse endocrine related effects caused by the substance, and establish a dose-response relationship between the dose and the E, A, or T effect.

Between October 2009 and February 2010, EPA issued test orders/data call-ins for the first group of 67 chemicals, which contains 58 pesticide active ingredients and nine inert ingredients. This list of chemicals was selected based on the potential for human exposure through pathways

such as food and water, residential activity, and certain post-application agricultural scenarios.

This list should not be construed as a list of known or likely endocrine disruptors.

CPPA is not among the group of 58 pesticide active ingredients on the initial list to be screened under the EDSP. Under FFDCA section 408(p) the Agency must screen all pesticide chemicals. Accordingly, EPA anticipates issuing future EDSP test orders/data call-ins for all pesticide active ingredients.

For further information on the status of the EDSP, the policies and procedures, the list of 67 chemicals, the test guidelines and the Tier 1 screening battery, please visit our website: http://www.epa.gov/endo/.

# 2. Dose Response Assessment

Because no toxicological endpoints were identified for this active ingredient, a dose response assessment was not required.

# 3. Drinking Water Exposure and Risk Characterization

CPPA is derived from NOM which is already present as an undesirable component of drinking water due to organoleptic effects. No significant exposure via drinking water beyond what is already present, is expected when CPPA is used according to the product label directions. The active ingredient biodegrades rapidly (half-life = 25.7 days) in the environment, is applied at low application rates and is not directly applied to water; therefore, residues of CPPA are unlikely to accumulate in drinking water or exceed the levels at which NOM is already present. In the unlikely event that exposure to the active ingredient via drinking water does occur, the health risk(s) would be expected to be minimal based on the lack of acute oral toxicity of CPPA and the fact that CPPA (humic acids, fulvic acids and tannins) are substances that are ubiquitous in soil and water. Further, maximum expected EEC's following application of CPPA according to the maximum proposed seasonal application rate are expected to be < 2 ppm on all terrestrial matrices and < 0.0004 ppm in aquatic matrices.

# 4. Occupational, Residential, School and Day Care Exposure and Risk Characterization

#### a. Occupational Exposure and Risk Characterization

An occupational exposure assessment was not conducted for CPPA, and is not required. Appropriate PPE requirements on the label will mitigate any potential exposure to applicators and/or handlers. Additionally, no relevant toxicological endpoints have been identified. Based on the data and information available to the Agency, anticipated exposure is not likely to result in unreasonable risk to humans.

# b. Residential, School and Day Care Exposure and Risk Characterization

Based on current label use directions, residential, school, and daycare exposure is not expected. Risks associated with this exposure are not anticipated.

# 5. Aggregate Exposure from Multiple Routes Including Dermal, Oral, and Inhalation

There is reasonable certainty that no harm to the U.S. population will result from aggregate exposure to CPPA. This includes all exposures for which there is reliable information. EPA arrived at this conclusion based on the lack of toxicity of this active ingredient and that CPPA is a complex mixture of naturally occurring organic matter comprised primarily of humic acids, fulvic acids and tannins. The risks from aggregate exposure via the oral, dermal, and inhalation routes are a compilation of three low-risk exposure scenarios and are negligible. Maximum expected EEC's following application of CPPA according to the maximum proposed seasonal application rate are expected to be < 2 ppm on all terrestrial matrices and < 0.0004 ppm in aquatic matrices.

#### 6. Cumulative Effects

Pursuant to FFDCA section 408(b)(2)(D)(v), EPA has considered available information concerning the cumulative effects of CPPA residues and other substances that have a common mechanism of toxicity. No toxicological endpoints have been established for exposure to CPPA; therefore, cumulative effects with other substances that share a common mechanism of toxicity are not expected.

# 7. Risk Characterization

The Agency considered human exposure to CPPA in light of the relevant safety factors in FQPA and FIFRA. A determination has been made that no unreasonable adverse effects to the U.S. population in general, and to infants and children in particular, will result from the use of CPPA when label instructions are followed.

#### C. Environmental Assessment

# 1. Ecological Hazards

Adequate nontarget toxicology data/information is available to support registration of CPPA with the submission of nontarget toxicology data from the open literature. All nontarget toxicology data requirements for CPPA have been **satisfied**.

Based on the data/information, CPPA is moderately toxic to birds on an acute oral basis (>100 ppm), practically non-toxic to birds on a dietary basis (> 5000 ppm to 30000 ppm), practically non-toxic to moderately toxic to fish (species dependent, 5.6 to 107.2 ppm), and practically non-toxic to aquatic invertebrates (248 ppm). Data were not submitted for terrestrial plants; however,

they are exposed to CPPA-like substances at a level much higher than would occur via product application (< 2 ppm) on a continual basis. This exposure occurs primarily via naturally occurring soil organic matter (humic/fulvic acids and tannins). Humic and fulvic acids are ubiquitous in the environment as soil organic matter, and comprise 0.74% to 9.9% (approximately 7400 ppm to 99000 ppm) of mineral soils in the United States (Brady, 1974). Tannins are widely distributed in plants (Cornell, 2009), although content will vary considerably from species to species, and tannins are synthesized as defensive substances against insect predation. Aquatic plants also are continually exposed to dissolved, water soluble CPPA-like substances in the water, although the natural water content will vary by location. Available data indicate that tannins stimulate aquatic plant growth at low levels of exposure (0.3 to 3 ppm) and act as an algistat at approximately 5 to 30 ppm (Nicola et. al., 2004). Exposure of aquatic plants to CPPA following product application to a terrestrial crop via runoff (< 0.0004 ppm) is orders of magnitude lower than any known non-definitive endpoints.

For more information regarding nontarget organism toxicity data requirements, refer to Table 4 in Appendix A.

#### 2. Environmental Fate and Ground Water Data

Environmental fate and groundwater data are not required at this time because the results of the nontarget organism toxicity assessment (Tier I data requirements) did not trigger these Tier II data requirements.

# 3. Ecological Exposure and Risk Characterization

The Risk Quotients (RQ's) for non-target birds, non-target fish, non-target aquatic invertebrates, and non-target plants are all < 0.01 and are well below any levels of concern (LOC's) for the aforementioned taxa.

For more information regarding nontarget organism toxicity data requirements, refer to Table 4 in Appendix A.

## 4. Endangered Species Assessment

The Risk Quotients (RQ's) for non-target birds, non-target fish, non-target aquatic invertebrates, and non-target plants are all < 0.01 and are well below any LOC's for the aforementioned taxa, including threatened and endangered species

For more information regarding nontarget organism toxicity data requirements, refer to Table 4 in Appendix A.

#### D. Efficacy Data

Product performance data must be developed for all pesticides to ensure that pesticide products will perform as intended and that unnecessary pesticide exposure to the environment will not

occur as a result of the use of ineffective products. The Agency reserves the right to require on a case-by-case basis, submission of efficacy data for any pesticide product registered or proposed for registration that are intended to be used to control a pest of significance public health importance and a public health pest as defined in FIFRA section 28(d) and section 2(nn). For further guidance on product performance requirement, refer to Pesticide Registration Notice (PR) Notices 96-7, 2002-1 and Explanation of Statutory Framework for Risk-Benefit Balancing for Public Health Pesticides (<a href="http://www.epa.gov/PR\_Notices/pr2002-1.pdf">http://www.epa.gov/PR\_Notices/pr2002-1.pdf</a>) and (<a href="http://www.epa.gov/pesticides/health/risk-benefit.htm">http://www.epa.gov/PR\_Notices/pr2002-1.pdf</a>) and (<a href="http://www.epa.gov/pesticides/health/risk-benefit.htm">http://www.epa.gov/PR\_Notices/pr2002-1.pdf</a>) and (<a href="http://www.epa.gov/pesticides/health/risk-benefit.htm">http://www.epa.gov/PR\_Notices/pr2002-1.pdf</a>) and (<a href="http://www.epa.gov/pesticides/health/risk-benefit.htm">http://www.epa.gov/PR\_Notices/pr2002-1.pdf</a>) and (<a href="http://www.epa.gov/pesticides/health/risk-benefit.htm">http://www.epa.gov/pesticides/health/risk-benefit.htm</a>).

The EP submitted with this new active ingredient did not list pests of significance public health importance or a public health pest as defined in FIFRA section 28(d) and section 2(nn). Therefore, product performance (efficacy) was not evaluated.

#### V. RISK MANAGEMENT DECISION

# A. Determination of Eligibility for Registration

Section 3(c)(5) of FIFRA provides for the registration of a new active ingredient if it is determined that: (A) its composition warrants proposed claims; (B) its labeling and other materials comply with the requirements of FIFRA; (C) it will perform its intended function without unreasonable adverse effects on the environment; and (D) when used in accordance with widespread and commonly recognized practice, it will not generally cause unreasonable adverse effects on the environment.

The four criteria of the Eligibility Determination for Pesticidal Active Ingredients are satisfied by the science assessments supporting products containing the technical grade active ingredient, CPPA. Such products are not expected to cause unreasonable adverse effects. Therefore, CPPA as a technical grade active ingredient is eligible for registration for the labeled uses.

## B. Regulatory Decision

The data submitted fulfill the registration requirements of CPPA for use as a plant growth regulator on field and greenhouse crops, fruits, nuts, vines, and ornamentals to improve germination and seedling development, stimulate root and shoot growth, increase chlorophyll content, improve stress resistance and increase yields. Refer to Appendix B for product-specific information.

## Conditional/Unconditional Registration

All data requirements are fulfilled, and EPA determined that an unconditional registration of CPPA is appropriate.

#### C. Environmental Justice

EPA seeks to achieve environmental justice—the fair treatment and meaningful involvement of all people regardless of race, color, national origin, or income—with respect to the development, implementation, and enforcement of environmental laws, regulations, and policies. At this time, EPA does not believe that use of CPPA pesticide products will cause harm or a disproportionate impact on at-risk communities. For additional information regarding environmental justice issues, please visit EPA's website at

http://www.epa.gov/compliance/environmentaljustice/index.html.

# VI. ACTIONS REQUIRED BY REGISTRANTS

EPA evaluated all data submitted in connection with the registration of the CPPA pesticide products and determined that these data are sufficient to satisfy current registration data requirements. At this time, no additional data must be submitted to EPA for these particular products. For new uses and/or changes to existing uses, EPA may require additional data.

Notwithstanding the information stated in the previous paragraph, it should be clearly understood that certain specific data are required to be reported to EPA as a requirement for maintaining the Federal registration for a pesticide product. A brief summary of these types of data are listed below.

# A. Reporting of Adverse Effects

Pursuant to FIFRA section 6(a)(2), reports of all incidents of adverse effects to the environment must be submitted to EPA.

# B. Reporting of Hypersensitivity Incidents

Additionally, all incidents of hypersensitivity (including both suspected and confirmed incidents) must be reported to the Agency under the provisions of 40 CFR Part 158.2050(d).

# VII. Appendix A. Data Requirements (40 CFR Part 158-Subpart U)

\*NOTE: Master Record Identification (MRID) numbers listed in the following tables are representative of supporting data/information for the original registration of the product containing this active ingredient. Subsequent to this registration, there may be additional MRIDs that support registration of other products containing this active ingredient.

PARILL A Physical and Chemical Properties Stimuleted for the Technical Grade Active Agreeless and Chemical Chemical Chemical Chemical Chemical Communications of Chemical Communications and Communication Communications of Communication Communications (Communication) and Chemical Chemical Communications of Communications of Chemical Che

OCSPP Guideline No.	Property	Description of Result	MRID	
830.6302	Color	Dark brown to black	48105301	
830.6303	Physical State	Liquid	48105301	
830.6304	Odor	Slightly sweet to peanut oil	48105301	
830.6313	Stability to Normal and Elevated Temperatures, Metals and Metal Ions	Stable at ambient &elevated temperatures.	48105301	
830.6315	Flammability	Not applicable; product is an aqueous liquid	48105301	
830.6317	Storage Stability	Reported to be stable for 2 years.	48105301	
830.6319	Miscibility	Not applicable	48105301	
830.6320	Corrosion Characteristics	Reported to have the same corrosion characteristics as water.		
830.7000	pH	7.02 (7.00 listed on CSFs)	48105301	
830.7050	UV/Visible Light Absorption	No data 4810530		
830.7100	Viscosity	Same as water 48105301		
830.7200	Melting Point/Range	Not applicable	48105301	
830.7220	Boiling Point/Range	100°C	48105301	
830.7300	Density	1.02 - 1.06 at 20 °C	48105301	
830.7520	Particle Size, Fiber Length and Diameter Distribution	Not applicable	48105301	
830.7550	Partition Coefficient (n-		48105301	
830.7560	Octanol/Water)	Not Applicable		
830.7570		II III DESCRIPTION III I		
830.7840	Water Solubility	100% soluble	48105301	
830.7950	Vapor Pressure	>1 at 100 °C	48105301	

OCSPP Guideline No.	Property	Description of Result	MRID
830.6302	Color	Dark brown	48456501
830.6303	Physical State	Liquid	48456501
830.6304	Odor	Mild	48456501
830.6313	Stability to Normal and Elevated Temperatures, Metals and Metal Ions	Product will not normally contact metal ions during manufacture, storage or use.	48456501
remaints.	// as terrords on tree	Stability to elevated temp. study	

TABLE 2. Physical and Chemical Properties Submitted for the Technical Grade Active
Ingredient/Manufacturing-use Product (TGAI/MP) Carbon Power Concentrate (EPA File Symbol No. 84846G)

OCSPP Guideline No.	Property	Description of Result	MRID
CLEM	thend to mitginest!	in progress	CUPF Gold
830.6314	Oxidation/Reduction	Not Applicable; Components are not known to be strong oxidizing or reducing agents	48456501
830.6315	Flammability	Not applicable; product is an aqueous liquid	48456501
830.6316	Explodability	Not applicable	48456501
830.6317	Storage Stability	Study in progress	48456501
830.6319	Miscibility	Not applicable	48456501
830.6320	Corrosion Characteristics	Study in progress	48456501
830.7000	рН	6.75	48456501
830.7050	UV/Visible Light Absorption	pH Max Absorbance Neutral 0.748 Acidic 0.722 Basic 0.788	48456501
830.7100	Viscosity	1.09 centipoise @ 25 °C 0.796 centipoise @ 41 °C	48456501
830.7200	Melting Point/Range	Not applicable	48456501
830.7220	Boiling Point/Range	100 °C 484565	
830.7300	Density	1.010 g/cm <sup>3</sup> (8.43 lb/gal) @ 25 °C 1.002 g/cm <sup>3</sup> (8.43 lb/gal) @ 41 °C	
830.7370	Dissociation Constants in water	Not Applicable	48456501
830.7520	Particle Size, Fiber Length and Diameter Distribution	Not applicable	48456501
830.7550 830.7560 830.7570	Partition Coefficient (n- Octanol/Water)	Not Applicable	48456501
830.7840	Water Solubility	100% soluble	48456501
830.7950	Vapor Pressure	Approx. equal to water	48456501

Study/OPPTS Guideline No.	Results	Toxicity Category/Description	MRID
Acute oral toxicity (rat) (870.1100)	>5000 mg/kg	IV	47916001
Acute dermal toxicity (rat) (870.1200)	>5050 mg/kg	IV	47916002
Acute inhalation toxicity (rat) (870.1300)	>2.16 mg/L	IV	47916003
Primary eye irritation (rabbit) (870.2400)	No symptoms observed at any time post- instillation Non-irritating	IV 100	47916004
Primary dermal irritation (rabbit)	Erythema and edema were not observed at	IV	47916005

Table 3. Mammalian Toxicology I Symbol No. 84846-G). (40 CFR	Toxicology Data Requirements for the Manufacturing-use Product (MP) Carbon Power (EPA Fig.). (40 CFR § 158.2050)			
Study/OPPTS Guideline No.	Results	Toxicity Category/Description	MRID	
(870.2500)	any time during the study Non-irritating	LOg Cg Carle	Tik, KI	
Dermal sensitization (guinea pig) (870.2600)	No observable symptoms	Not a Sensitizer	47916006	

Table 4. Mammalian Toxicology Data Requirements for the Technical Grade Active Ingredient/Manufacturing-use Product (TGAI/MP) Carbon Power Concentrate (EPA File Symbol No. 84846-G) (40 CFR § 158.2050) Study Type/OCSPP Species MRID LD<sub>50</sub>/LC<sub>50</sub>/Results **Toxicity** Guideline NOAEL =1000 ppm HA1 Subchronic toxicity only Condie et. al.,  $NOAEL = 500 ppm HA + Cl^2$ with HA+Cl at 1000 1985 rat LOAEL = 1000 ppm HA+Clppm based on reduced 90-Day Oral Toxicity wgt gain. (OCSPP 870.3100)  $NOAEL = 1000 \text{ ppm HA}^1, HA+Cl^2, \text{ or}$ rat No subchronic toxicity Daniel et. al., HA+Cl+O<sup>3</sup> at doses tested 1991  $NOAEL = 119 \text{ mg } GA^4/\text{kg bw males}$ No subchronic toxicity rat  $LOAEL = 357^5 \text{ mg GA/kg bw males}$ at 119 mg GA<sup>4</sup>/kg bw Niho et al., NOAEL = 128 mg GA/kg bw females males and 128 mg 2001  $LOAEL = 2975^5 \text{ mg GA/kg bw females}$ GA/kg bw females 90-day Dermal Toxicity Waiver requested No repeated dermal (OCSPP 870.3250) exposure expected based on use pattern 90-day Inhalation Waiver requested No repeated inhalation (OCSPP 870.3465) exposure expected based on use pattern Combined Chronic No chronic effects on Van Duuren  $NOAEL = 500 \text{ ppm } HA^1 \text{ or } HA+Cl^2 \text{ in}$ Mice Toxicity/Carcinogenicity weight gain or incidence et. al., 1986 (OCSPP 870.4300) drinking water for 24 months of tumors relative to controls No maternal toxicity; no Meyer and  $NOAEL = 40000 \text{ ppm } TA^6 \text{ in diet}$ Prairie voles developmental effects Richardson, 1993 Prenatal Development on pups (OSCPP 870.3700) 800 ppm HA<sup>1</sup> to gestating dams 800 ppm HA to dams & pups up to 21 d No maternal toxicity; no Smith et. al., developmental effects postpartum Rat 1986 1000 ppm HA to pups up to 41 d on pups postpartum 500 ppm HA<sup>1</sup> or HA+Cl<sup>2</sup> or HA+Cl+O<sup>3</sup> Not mutagenic at dose Van Duuren et. al., 1986 typhimurium tested Up to 2000000 ug HA<sup>1</sup>/plate from 3 Not mutagenic at dose S. Bernacchi et. **Bacterial Reverse Mutation** different sources typhimurium tested al., 1996 a & b Test  $50 \text{ ppm SFA}^7$ , SFA+ Cl<sup>8</sup>, SFA + O<sup>9</sup>, or No mutagenicity in SFA Kowbel et. al., S. (OCSPP 870.5100) SFA+Cl+O10 and ozonated SFA 1984a,b typhimurium Up to 100 ug TA<sup>6</sup>/plate Not mutagenic at dose S. Mohtashatyphimurium tested mipur and

Table 4. Mammalian Toxicology Data Requirements for the Technical Grade Active Ingredient/Manufacturing-use Product (TGAI/MP) Carbon Power Concentrate (EPA File Symbol No. 84846-G) (40 CFR § 158.2050)

Study Type/OCSPP Guideline	LD <sub>50</sub> /LC <sub>50</sub> /Results	Species	Toxicity	MRID
THE REPORT OF	representation of the contract of	althornes alt.	(30) Admirgo mino (Admiro Adm	Norpoth, 1984
	Up to 5000 ug/plate of GA <sup>4</sup> , TA <sup>6</sup> , or GT <sup>11</sup>	S. typhimurium	Not mutagenic at doses tested	Rashid et. al., 1985
	Up to 3000 ug/plate of TA <sup>6</sup> , EA <sup>12</sup> , GA <sup>4</sup> , and PG <sup>13</sup>	S. typhimurium	Not mutagenic at doses tested	Chen and Chung, 2000
In Vitro Mammalian Gene Mutation Test; and In Vitro Mammalian Chromosome	125 to 500 ppm HA <sup>1</sup> for 2 or 24 hours NOEC = 125 ppm LOEC = 250 ppm	Cultured human lymphocytes	Significant increase in SCE <sup>14</sup> at 250 and 500 ppm; no effect at 125 ppm.	Ribas et. al., 1997
Aberration Test (OSCPP 870.5300 & 870.5375)	2.5 to 10 ppm LHA <sup>1</sup> or SHA <sup>1</sup> for 2 hours NOEC = 10 ppm	Cultured human lympho- blastoid cells	No genotoxic effects of LHA or SHA alone or in combination at doses tested	Ferrara et. al., 2006

and less	Humic acid (HA); Leonardite HA (LHA); Soil HA	(SHA) NOAEL = No Observed	Adverse Effect Level
2	Chlorinated humic acid	NOEC = No Observed Effect Concentration	
3	Chlorinated and ozonated humic acid	LOAEL = Lowest Observed Adverse Effect Level	
4	Gallic acid (a hydrolyzed tannin)	LOEC = Lowest Observe	ed Effect Concentration
5	Interpolated by reviewer	U. Printed The state of the sta	
6	Tannic acid		
7	Soil fulvic acid		
8	Chlorinated soil fulvic acid		
9	Ozonated soil fulvic acid		
10	Chlorinated and ozonated fulvic acid		
11	Gallotannin		
12	Elagic acid ( a hydrolyzed tannin)		
13	Propyl gallate ( a hydrolyzed tannin)		
14	Sister chromatid exchange		

Study Type/OCSPP Guideline	LD <sub>50</sub> /LC <sub>50</sub> /Results	Species	Toxicity Category	MRID or Citation
Avian Acute Oral Toxicity OCSPP 850.2100	>100 mg/kg (gallic acid) <sup>1</sup>	Red-winged blackbird	Moderately toxic	Schafer et. al., 1983.
	>30000 ppm (tannins)	poultry	Practically non-toxic	Cornell Univ., 2009.
Avian Dietary Toxicity OCSPP 870.2200	5000 ppm (tannins; depressed growth and egg production)	poultry	Practically non-toxic	Cornell Univ., 2009
	1500-2500 ppm for 42 d (humic acid increased broiler wgt)	Poultry	Not Applicable	Islam et. al., 2005.
	96 hr $LC_{50} = 50 \text{ ppm}^2$	Carp (Cyprinus carpio L.)	Slightly toxic	Temmink et al. 1989.
Freshwater Fish LC <sub>50</sub> OCSPP 850.1075	96 hr $LC_{50} = 5.8 \text{ ppm}^3$ 96 hr $LC_{50} = 5.6 \text{ ppm}^3$ 96 hr $LC_{50} = 7.0 \text{ ppm}^3$	Fancy Carp (Cyprinus carpio L.) guppy (Poecilia reticulate) Siamese Fighting fish (Beta splendens)	Moderately non-toxic	Chansue and Assawawong- kasem, 2008.
	96 hr LC <sub>50</sub> = 30 <sup>4</sup> or 107.2 ppm <sup>5</sup>	Tilapia (Oreochromis mossabica)	Slightly toxic to Practically non-toxic	Saha and Kaviraj, 1996.
Aquatic Invertebrate Toxicity OCSPP 850.1010	EC <sub>50</sub> = 248 ppm (immobilization) NOEC = 175 ppm	Daphnids	Practically non-toxic	Nicola, et. al., 2004.
Non-Target Plants	Algae treated with 0.03 to 30 ppm tannins <sup>6</sup>			

OCSPP 850.4100-4150 (as applicable)	Growth stimulation at up to 0.3 ppm (S. capricornutum) or up to 3 ppm (D. tertiolecta) Growth inhibited at approx. 5 <sup>7</sup> to approx. 20 <sup>7</sup> ppm, respectively	Marine (S. capricornutum) and freshwater algae (D. tertiolecta), respectively	No mortality observed	Nicola, et. al., 2004.
Non-Target Insects OCSPP 850.4350	>25 ug/bee NOEC = 2.5 ug/bee	Honey bee (Apis mellifera)	Practically non-toxic	48795201

Gallic acid is a common tannin

- Extract of Norway Spruce bark (50-60% tannins, 35% sugars, 10% non-tannin monomers, 5% resins)
- Water extract of Indian almond (*Terminalia catappa* L.) leaves.
- 4 Extract of Cinchona bark
- 5 Analytical grade tannic acid
- Fresh tannin water extract of Mimosa
- Interpolated by the reviewer from Fig 8 in Nicola et. al. (200

	and quantied over the	

# VIII. Appendix B

For product specific information, please refer to <a href="http://www.epa.gov/pesticides/pestlabels">http://www.epa.gov/pesticides/pestlabels</a>.

# IX. Appendix C

#### REFERENCES

Anonymous. 2006. Researchers study role of natural organic matter in the environment. Science Daily. <a href="http://www.sciencedaily.com/releases/2006/12/061211221222.htm">http://www.sciencedaily.com/releases/2006/12/061211221222.htm</a> (Accessed 11/10/2010)

ASA Analytics. 2010. Natural organic matter (NOM) in water. http://www.anaanalytics.com/natural-organic-matter.php (Accessed 11/10/2010)

Sannigrahi, P. 2005. Composition and cycling of natural organic matter: In sights from NMR spectroscopy. Thesis presented to the Faculty of the School of Earth and Atmospheric Sciences, Georgia Institute of Technology. Date Approved: November 16, 2005. (<a href="http://etd.gatech.edu/theses/available/etd-11272005-094111/unrestricted/sannigrahi">http://etd.gatech.edu/theses/available/etd-11272005-094111/unrestricted/sannigrahi</a> poulomi 200512 phd.pdf (Accessed 11/10/2010).

Nova Scotia Environment (NSE). 2008. The drop on humic substances. <a href="http://www.gov.ns.ca/nse/water/docs/droponwaterFAQ\_HumicSubstances.pdf">http://www.gov.ns.ca/nse/water/docs/droponwaterFAQ\_HumicSubstances.pdf</a> 03/2008 Update; Accessed 11/18/2010.

UNESCO. 2010. Characterization of natural organic matter in drinking water. Institute for Water Education. <a href="http://www.unesco-ihe.org/About/Academic-departments/Urban-Water-and-Sanitation/Core-Groups/Water-Supply-Engineering-WSE/Research/PhD-Research2/Characterization-of-natural-organic-matter-in-drinking-water">http://www.unesco-ihe.org/About/Academic-departments/Urban-Water-and-Sanitation/Core-Groups/Water-Supply-Engineering-WSE/Research/PhD-Research2/Characterization-of-natural-organic-matter-in-drinking-water</a> (Accessed 11/10/2010).

Weber, J. 2010. Definition of Soil Organic Matter. Humin Tech: Agriculture. <a href="http://www.humintech.com/001/articles/article\_definition\_of\_soil\_organic\_matter.html">http://www.humintech.com/001/articles/article\_definition\_of\_soil\_organic\_matter.html</a> (Accessed 11/18/2010).

Bernacchi, F., I. Ponzanelli, R. Barale, and N. Loprieno. 1996a. Mutagenic activity of some coal-derived humic compounds evaluated by the Ames test. Mutation Research 369: 107-112.

Bernacchi, F., I. Ponzanelli, M. Minunni, A, Falezza, N. Loprieno, and R. Barale. 1996b. Mutagenesis 11(5): 467-469.

Brady, N. C. 1974. The Nature and Properties of Soils. 8<sup>th</sup> Edition. Macmillan Publishing Co., Inc. New York. ISBN 0-02-31350-3.

Chen, S-C., and K-T. Chung. 2000. Mutagenicity and antimutagenicity studies of tannic acid and its related compounds. Food and Chemical Toxicology 38: 1-5.

- Chowdhury, S. P., S. Khanna, S. C. Verma, and A. K. Tripathi. Molecular diversity of tannic acid degrading bacteria from tannery soil. Journal of Applied Microbiology 97(6): 1210-1219.
- Condie, L. W., R. D. Laurie, and J. P. Bercz. 1885. Subchronic toxicology of humic acid following chlorination in the rat. Journal of Toxicology and Environmental Health 15: 305-314. Daniel, F. B., M. Robinson, H. P. Ringhand, J. A. Stober, N. P. Page, and G. R. Olsen. 1991. Environmental Science and Technology 25(1): 93-98.
- Dekker, J. and C. E. Medlen. 2003. Fulvic acid and its use in the treatment of various conditions. United States Patent No. US 6,569,900 B1.
- European Agency for the Evaluation of Medicinal Products (EMEA). 1999. Humic acids and their sodium salts. Committee for Veterinary Medicinal Products. EMEA/MRL/554/9 FINAL. February 1999.
- http://www.ema.europa.eu/docs/en\_GB/document\_library/Maximum\_Residue\_Limits\_-Report/2009/11/WC500014416.pdf
- Ferrara, G., E. Loffredo, N Senesi, and R. Marcos. 2006. Humic acids reduce the genotoxicity of mitomycin C in the human lymphoblastoid cell line TK6. Mutation Research 603: 22-32.
- Kowbel, D. J., M. Malaiyandi, V. Paramasigamani, and E. R. Nestmann. 1984. Chlorination of ozonated soil fulvic acid: Mutagenicity studies in Salmonella. The Science of the Total Environment 37: 171-176.
- Kowbel, D. J., S. Ramaswamy, M. Malayandi, and E. P. Nestmann. 1986. Environmental Mutagenesis 8: 253-262.
- Meyer, M. W., and C. Richardson. 1993. The effects of chronic tannic acid intake on prairie vole (Microtus ochrogaster) reproduction. Journal of Chemical Ecology 19(7): 1577-1585.
- Michael, G., E. L. George, and M. K. Smith. 1983. Developmental studies of model chlorinated humics in drinking water (abstr.). Toxicologist 3: 273.
- Niho, N., M. Shibutani, T. Tamura, K. Toyada, C. Uneyama, N. Takahashi, and M. Hirose. 2001. Subchronic toxicity of gallic acid by oral administration in F344 rats. Food and Chemical toxicology 39: 1063-1070.
- Rashid, K. A., I. T. Baldwin, J. C. Babish, J. C. Schultz, and R. O. Mumma. 1985. Mutagenicity tests with gallic acid and tannic acid in the salmonella/mammalian microsome assay. Journal of Environmental Science and Health, Part B 20(2): 153-165.
- Ribas, G., E. Carbonell, A. Creus, N. Xamena, and R. Marcos. 1997. Genotoxicity of humic acid in cultured human lymphocytes and its interaction with the herbicides alachlor and maleic hydrazide. Environmental and Molecular Mutagenesis. 29: 272-276.
- Smith, M. K., H. Zenick, and E. L. George. 1986. Reproductive toxicology of disinfection by-

products. Environmental Health Perspectives 69: 177-182.

Steffen, K. T., A. Hatakka, and M. Hofrichter. 2002. Degradation of humic acids by the litter decomposing Basidiomycete Collybia dryophila. Applied Environmental Microbiology 68(7): 3442-3448.

Ueno, H., T. Segawa, K. Nakamuro, Y. Sayato, and S. Okada. 1989. Mutagenicity and identification of products formed by aqueous ozonation of humic acids of different origins. Chemosphere 19(12): 1843-1852.

USEPA. 2001. Generic Estimated Environmental Concentration Model (GENEEC) Version 2.0. Tier I Screening Model for Pesticide Aquatic Ecological Exposure Assessment. Environmental Fate and Effects Division (EFED)

USEPA. 2008. Terrestrial Exposure Model (T-REX) Version 1.4.1. Environmental Fate and Effects Division (EFED) Terrestrial Biology and Exposure Technical Teams. October 9, 2008.

Anonymous, 2012. Development of Bees – From the Egg to the Bee; Development of the Honey Bees Table. <a href="https://www.bee-info.com/biology-bee/development-tabular.html">www.bee-info.com/biology-bee/development-tabular.html</a> Accessed 08/28/2012.

#### REVIEWS AND OTHER REFERENCES

U.S. EPA. 2010. Memorandum from Russell S. Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review in Support of the Registration of Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, and End-Use Product (EP), Respectively Containing 2% and 0.4% Polymeric Polyhydroxy Acid As Their Active Ingredient. U.S. Environmental Protection Agency Office of Pesticide Programs. March 01,, 2010.

U.S. EPA. 2010. Memorandum from Russell S. Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review in Support of the Registration of Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, an End-Use Product (EP), Respectively Containing 2% and 0.4% of the New Active Ingredient, Complex Polymeric Polyhydroxy Acids. U.S. Environmental Protection Agency Office of Pesticide Programs. December 20, 2010.

U.S. EPA. 2011. Memorandum from Russel Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review of Product Chemistry in Support of the Second Resubmission of the Registration of Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, an End-Use Product (EP), Respectively Containing 0.9% and 0.18% of the New Active Ingredient, Complex Polymeric Polyhydroxy Acids (CPPA); and a Tolerance Exemption. U.S. Environmental Protection Agency Office of Pesticide Programs. November 16, 2011.

U.S.EPA. 2012. Memorandum from Russel Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review in Support of the Second Resubmission of the Registration of

Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, an End-Use Product (EP), Respectively Containing 2% and 0.4% of the New Active Ingredient, Complex Polymeric Polyhydroxy Acids; and a Tolerance Exemption. Review of Non-Target Organism Data, Information, and Waiver Requests; Non-target Organism Hazard Assessment and Endangered Species Risk Assessment. U.S. Environmental Protection Agency Office of Pesticide Programs. February 03, 2012.

U.S.EPA. 2012. Memorandum from Russel Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review in Support of the Second Resubmission of the Registration of Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, an End-Use Product (EP), Respectively Containing 4% and 0.4 % of the New Active Ingredient, Complex Polymeric Polyhydroxy Acids; and a Tolerance Exemption. Review of Tier I Toxicity Data, Information, and Waiver Requests. U.S. Environmental Protection Agency Office of Pesticide Programs. March 01, 2012.

U.S.EPA. 2012. Memorandum from Russell Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review in Support of the Registration of Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, an End-Use Product (EP), Respectively Containing 0.9% and 0.18% of the New Active Ingredient, Complex Polymeric Polyhydroxy Acids; and a Tolerance Exemption. Response to Product Chemistry Deficiencies, Tier I Toxicity Deficiencies, and Tier I Non-Target Organism Deficiencies. U.S. Environmental Protection Agency Office of Pesticide Programs. August 02, 2012.

U.S.EPA. 2012. Memorandum from Russell Jones, Ph.D., Senior Biologist to Menyon Adams, Biologist. Science Review in Support of the Registration of Carbon Power Concentrate, a Manufacturing Use Product (MP) and Carbon Power, an End-Use Product (EP), Respectively Containing 0.90% and 0.18% of the New Active Ingredient, Complex Polymeric Polyhydroxy Acids; and a Tolerance Exemption. Review of Non-Target Insect Study and Endangered Species (Insect) Risk Assessment. U.S. Environmental Protection Agency Office of Pesticide Programs. August 28, 2012.

## X. GLOSSARY OF ACRONYMS AND ABBREVIATIONS

a.i. active ingredient

BPPD Biopesticides and Pollution Prevention Division

BRAD Biopesticide Registration Action Document

bw body weight

CBI Confidential Business Information

CFR Code of Federal Regulations

cm<sup>3</sup> cubic centimeter

CSF Confidential Statement of Formula

°C degrees Celsius

EC<sub>50</sub> median effective concentration. A statistically derived single concentration in environmental medium that can be expected to cause an effect in 50% of the test animals when

administrated by the route indicated (inhalation). It is expressed as a concentration in air or water (e.g. mg/L).

EDSP Endocrine Disruptor Screening Program

EDSTAC Endocrine Disruptor Screening and Testing Advisory Committee

EP end-use product

EPA Environmental Protection Agency (the "Agency")

FDA Food and Drug Administration

FFDCA Federal Food, Drug, and Cosmetic Act

FIFRA Federal Insecticide, Fungicide, and Rodenticide Act

FOPA Food Quality Protection Act

FR Federal Register

g gram

ha hectare

kg kilogram

Kow octanol-water partition coefficient

L. lite

LC<sub>50</sub> median lethal concentration. A statistically derived single concentration in air or water that can be expected to cause death in 50% of the test animals when administrated by the route indicated (inhalation and environment). It is expressed as a concentration in air or water (e.g. mg/L).

LD<sub>50</sub> median lethal dose. A statistically derived single dose that can be expected to cause death in 50% of the test animals when administered by the route indicated (oral and dermal). It is expressed as a weight of substance per unit weight of animal (e.g., mg/kg).

MRID No. Master Record Identification Number

mg milligram

mPa millipascal

mL milliliter

MP manufacturing-use product

N/A not applicable

NE "No Effect"

NIOSH National Institute for Occupational Safety and Health

nm nanometer

NOEL no-observed-effect-level

NOF notice of filing

NOR notice of receipt

OPP Office of Pesticide Programs

OCSPP Office of Chemical Safety and Pollution Prevention

pa pascal

PPE personal protective equipment

PR Notice Pesticide Registration Notice

TGAI technical grade of the active ingredient

ug microgram

USDA United States Department of Agriculture

UV ultra-violet

# **Summary Report**

Registration #	Name	Status	Restricted Use Product	Company #	Company Name	Percent Active Ingredient	Active Ingredient
100-1451	APPEAR	Registered (16-Jul-2012)	N	100	SYNGENTA CROP PROTECTION, LLC	53.3	Mono- and di- potassium salts of phosphorous acid
100-1599	INOSCO	Registered (27-Jul-2016)	N	100	SYNGENTA CROP PROTECTION, LLC	54.5	Mono- and di- potassium salts of phosphorous acid
264-1054	FOLI-R-FOS 400 FUNGICIDE	Registered (28-Jul-2004)	N	264	BAYER CROPSCIENCE LP	45.5	Mono- and di- potassium salts of phosphorous acid
432-1522	ES TC006A	Registered (29-May-2012)	N	432	BAYER ENVIRONMENTAL SCIENCE	25.85	Mono- and di- potassium salts of phosphorous acid
1381-236	PHOSPHOROUS ACID SYSTEMIC FUNGICIDE	Registered (21-Feb-2008)	N	1381	WINFIELD SOLUTIONS, LLC	45.8	Mono- and di- potassium salts of phosphorous acid
1381-244	CONFINE EXTRA	Registered (23-Sep-2010)	N	1381	WINFIELD SOLUTIONS, LLC	53	Mono- and di- potassium salts of phosphorous acid
5905-563	HELENA PHOSPHOROUS ACID TECHNICAL FUNGICIDE	Registered (06-Apr-2007)	N	5905	HELENA CHEMICAL COMPANY	99.68	Phosphorous acid
5905-566	HM-0210-A SYSTEMIC PGR & FUNGICIDE	Registered (24-Jul-2007)	N	5905	HELENA CHEMICAL COMPANY		Indole-3- butyric acid
5905-566	HM-0210-A SYSTEMIC PGR & FUNGICIDE	Registered (24-Jul-2007)	N	5905	HELENA CHEMICAL COMPANY	56	Mono- and di- potassium salts of phosphorous acid
7946-26	ARBORFOS	Registered (01-Dec-	N	7946	J. J. MAUGET CO.	45.8	Mono- and di- potassium salts of

		2004)					phosphorous acid
7946-31	ARBORFOS HP	Registered (01-Oct- 2009)	N	7946	J. J. MAUGET CO.	45.8	Mono- and dipotassium salts of phosphorous acid
8622-68	CALIRUS 150	Registered (15-Nov-2004)	N	8622	ICL-IP AMERICA, INC.	.15	Copper sulfate pentahydrate
8622-68	CALIRUS 150	Registered (15-Nov- 2004)	N	8622	ICL-IP AMERICA, INC.	10.3	Mono- and dipotassium salts of phosphorous acid
19713-625	DREXEL PHITICIDE	Registered (15-Aug-2003)	N	19713	DREXEL CHEMICAL COMPANY	56.2	Mono- and dipotassium salts of phosphorous acid
19713-633	DREXEL PHOSPHOROUS ACID TECHNICAL	Registered (15-Aug-2003)	N	19713	DREXEL CHEMICAL COMPANY	98.5	Phosphorous acid
34704-924	RAMPART FUNGICIDE	Registered (25-Apr- 2006)	N	34704	LOVELAND PRODUCTS, INC.	53	Mono- and di- potassium salts of phosphorous acid
42519-22	PROPHYT	Conditionally Registered (19-Jan- 2001)	N	42519	LUXEMBOURG- PAMOL, INC.	54.5	Mono- and dipotassium salts of phosphorous acid
42519-24	VITAL	Conditionally Registered (04-Nov- 2002)	N	42519	LUXEMBOURG- PAMOL, INC.	54.5	Mono- and dipotassium salts of phosphorous acid
42519-29	VITAL-SIGN	Registered (13-Jun- 2006)	N	42519	LUXEMBOURG- PAMOL, INC.	53.3	Mono- and dipotassium salts of phosphorous acid
42519-30	VITALONIL	Conditionally Registered (13-Aug- 2008)	N	42519	LUXEMBOURG- PAMOL, INC.	16.7	Chlorothalonil
42519-30	VITALONIL	Conditionally Registered (13-Aug-	N	42519	LUXEMBOURG- PAMOL, INC.	38.9	Mono- and di- potassium salts of

		2008)					phosphorous acid
42519-31	CATAMARAN	Registered (08-Oct- 2008)	N	42519	LUXEMBOURG- PAMOL, INC.	38.9	Mono- and di- potassium salts of phosphorous acid
42519-31	CATAMARAN	Registered (08-Oct- 2008)	N	42519	LUXEMBOURG- PAMOL, INC.	16.7	Chlorothalonil
42519-32	PROPHYT-PHC	Registered (02-Apr- 2009)	N	42519	LUXEMBOURG- PAMOL, INC.	54.5	Mono- and di- potassium salts of phosphorous acid
42519-33	LBG-W	Registered (05-Mar- 2009)	N	42519	LUXEMBOURG- PAMOL, INC.	54.5	Mono- and di- potassium salts of phosphorous acid
42519-35	LBG-61	Conditionally Registered (13-Oct- 2010)	N	42519	LUXEMBOURG- PAMOL, INC.	3.3	Tebuconazole
42519-35	LBG-61	Conditionally Registered (13-Oct- 2010)	N	42519	LUXEMBOURG- PAMOL, INC.	49	Mono- and di- potassium salts of phosphorous acid
42519-36	POTASSIUM PHOSPHITE TECHNICAL	Registered (20-Jun- 2012)	N	42519	LUXEMBOURG- PAMOL, INC.	99	Mono- and di- potassium salts of phosphorous acid
42519-37	LPI-37	Registered (19-Nov- 2015)	N	42519	LUXEMBOURG- PAMOL, INC.	97.34	Mono- and di- potassium salts of phosphorous acid
42519-38	LBG-W-MUP	Registered (05-Jan- 2016)	N	42519	LUXEMBOURG- PAMOL, INC.	54.5	Mono- and di- potassium salts of phosphorous acid
48222-8	AGRO-K PHOS ACID TECHNICAL	Registered (06-Feb- 2012)	N	48222	AGRO-K CORPORATION	70	Phosphorous acid
48222-10	AGRO-K K-PHOS	Registered (21-Mar- 2014)	N	48222	AGRO-K CORPORATION	57	Mono- and di- potassium salts of phosphorous

							acid
55146-82	PHOSPHOROUS ACID TECHNICAL	Conditionally Registered (28-Sep- 2000)	N	55146	NUFARM AMERICAS, INC.	70	Phosphorous acid
55146-83	PHOSTROL AGRICULTURAL FUNGICIDE	Conditionally Registered (28-Sep- 2000)	N	55146	NUFARM AMERICAS, INC.	53.6	Mono- and di- potassium salts of phosphorous acid
68573-2	FOSPHITE FUNGICIDE	Conditionally Registered (27-Oct- 2000)	N	68573	JH BIOTECH INC	53	Mono- and di- potassium salts of phosphorous acid
69117-5	WHIPPET FUNGICIDE	Registered (13-Jan-2004)	N	69117	ARBORSYSTEMS, INC.	45.8	Mono- and di- potassium salts of phosphorous acid
70299-22	OXIPHOS	Registered (06-Sep- 2012)	N	70299	BIOSAFE SYSTEMS, LLC	14	Hydrogen peroxide
70299-22	OXIPHOS	Registered (06-Sep- 2012)	N	70299	BIOSAFE SYSTEMS, LLC	27.1	Mono- and di- potassium salts of phosphorous acid
70506-291	JETPHITER	Registered (04-Apr- 2012)	N	70506	UNITED PHOSPHORUS, INC	45.5	Mono- and di- potassium salts of phosphorous acid
70908-4	PHOS PRO FUNGICIDE	Registered (22-Oct- 2004)	N	70908	GROW MORE, INC.	55.45	Mono- and dipotassium salts of phosphorous acid
71962-1	AGRI-FOS 400	Conditionally Registered (05-Feb- 2002)	N	71962	LIQUID FERTILISER PTY. LTD. (TRADING AS AGRICHEM)	45.8	Mono- and di- potassium salts of phosphorous acid
71962-2	AGRI-FOS SYSTEMIC FUNGICIDE PLUS	Registered (10-Feb- 2015)	N	71962	LIQUID FERTILISER PTY. LTD. (TRADING AS AGRICHEM)	60.56	Mono- and di- potassium salts of phosphorous acid
73771-5	FUNGI-PHITE	Registered (21-Oct-	N	73771	VERDESIAN LIFE SCIENCES U.S.,	45.5	Mono- and di- potassium salts of

		2005)			LLC		phosphorous acid
73771-6	FUNGI-PHITE DF MUP	Registered (01-Jul-2010)	N	73771	VERDESIAN LIFE SCIENCES U.S., LLC	99	Mono- and dipotassium salts of phosphorous acid
73771-7	FUNGI-PHITE DF	Registered (01-Jul-2010)	N	73771	VERDESIAN LIFE SCIENCES U.S., LLC	99	Mono- and dipotassium salts of phosphorous acid
73771-8	MANCO-PHITE DF	Conditionally Registered (30-Sep- 2010)	N	73771	VERDESIAN LIFE SCIENCES U.S., LLC	50.02	Mancozeb
73771-8	MANCO-PHITE DF	Conditionally Registered (30-Sep- 2010)	N	73771	VERDESIAN LIFE SCIENCES U.S., LLC	31	Mono- and dipotassium salts of phosphorous acid
73771-9	FUNGI-PHITE MUP	Registered (07-Oct- 2011)	N	73771	VERDESIAN LIFE SCIENCES U.S., LLC	45.5	Mono- and di- potassium salts of phosphorous acid
73806-1	K-PHITE 7LP FUNGICIDE	Registered (26-Jul-2007)	N	73806	PLANT FOOD SYSTEMS, INC.	56	Mono- and dipotassium salts of phosphorous acid
73806-2	MAXIPHITE® FUNGICIDE	Conditionally Registered (16-Sep- 2002)	N	73806	PLANT FOOD SYSTEMS, INC.	20.4	Mono- and dipotassium salts of phosphorous acid
73806-2	MAXIPHITE® FUNGICIDE	Conditionally Registered (16-Sep- 2002)	N	73806	PLANT FOOD SYSTEMS, INC.	22.67	Dipotassium phosphate
74578-3	PHOSPHO-JET	Registered (09-Feb- 2006)	N	74578	ARBORJET, INC.	45.8	Mono- and di- potassium salts of phosphorous acid
82940-1	RESIST	Registered (13-Jun- 2006)	N	82940	ACTAGRO, LLC	57	Mono- and di- potassium salts of phosphorous acid
							Mono- and di-

minary report. I	togistration						
83416-1	RELIANT SYSTEMIC FUNGICIDE	Registered (22-Mar- 2012)	N	83416	QUEST PRODUCTS L.L.C.	45.8	potassium salts of phosphorous acid
83416-2	PHOSPHOROUS ACID TECHNICAL 70%	Registered (01-Nov- 2012)	N	83416	QUEST PRODUCTS L.L.C. 70		Phosphorous acid
86381-2	FRESHPROTECT	Registered (30-Nov- 2012)	N	86381	PIMI AGRO CLEAN TECH, LTD	5	Hydrogen peroxide
86381-2	FRESHPROTECT	Registered (30-Nov- 2012)	N	86381	PIMI AGRO CLEAN TECH, LTD	10.56	Mono- and di- potassium salts of phosphorous acid
86868-4	FIRST CHOICE PHORTRESS FUNGICIDE	Registered (13-Oct- 2009)	N	86868	OMEX AGRIFLUIDS, INC.	28.1	Mono- and di- potassium salts of phosphorous acid
86868-4	FIRST CHOICE PHORTRESS FUNGICIDE	Registered (13-Oct- 2009)	N	86868	OMEX AGRIFLUIDS, INC.	40.8	Potassium phosphate, monobasic

# **Summary Report**

Registration #	Name	Status	Restricted Use Product	Company #	Company Name	Percent Active Ingredient	Active Ingredient
82100-1	SIL- MATRIX	Registered (11-May-2006)	N	82100	PQ CORPORATION, C/O AG-CHEM CONSULTING	29	Potassium silicate
82100-2	TECHNICAL POTASSIUM SILICATE	Registered (12-May-2006)	N	82100	PQ CORPORATION, C/O AG-CHEM CONSULTING	99.4	Potassium silicate
84846-1	CARBON DEFENSE	Registered (18-Sep-2009)	N	84846	FBSCIENCES, INC.	11.14	Potassium silicate
88306-1	POTASSIUM SILICATE TECHNICAL	Registered (03-Jul- 2012)	N	88306	AGRI-NEO INC	99.4	Potassium silicate
88306-3	ATO CIDE GRANULAR	Registered (18-Sep-2014)	N	88306	AGRI-NEO INC	10	Potassium silicate
88306-3	ATO CIDE GRANULAR	Registered (18-Sep-2014)	N	88306	AGRI-NEO INC	50	Sodium percarbonate
88306-3	ATO CIDE GRANULAR	Registered (18-Sep- 2014)	N	88306	AGRI-NEO INC	20	Tetraacetylethylenediamine
88306-4	NEO-BOOST	Registered (10-Sep-2015)	N	88306	AGRI-NEO INC	17.89	Potassium silicate
88306-4	NEO-BOOST	Registered (10-Sep-2015)	N	88306	AGRI-NEO INC	9.99	Tetraacetylethylenediamine
88306-4	NEO-BOOST	Registered (10-Sep- 2015)	N	88306	AGRI-NEO INC	51	Sodium percarbonate

# **Summary Report**

Registration #	Name	Status	Restricted Use Product	Company #	Company Name	Percent Active Ingredient	Active Ingredient
34704-1055	CONSENSUS	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	.02	Indole-3- butyric acid
34704-1055	CONSENSUS	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	1	Chitosan
34704-1055	CONSENSUS	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	.04	Salicylic acid
34704-1056	CONSENSUS RTU	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	.0033	Indole-3- butyric acid
34704-1056	CONSENSUS RTU	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	.17	Chitosan
34704-1056	CONSENSUS RTU	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	.0067	Salicylic acid
34704-1057	SALICYLIC ACID TECHNICAL	Registered (06-Mar- 2012)	N	34704	LOVELAND PRODUCTS, INC.	98.7	Salicylic acid
73178-1	BIOPLUS ST	Registered (12-May- 2016)	N	73178	SECURITY SEED AND CHEMICAL, INC	.02	Indole-3- butyric acid
73178-1	BIOPLUS ST	Registered (12-May- 2016)	N	73178	SECURITY SEED AND CHEMICAL, INC	.04	Salicylic acid
73178-1	BIOPLUS ST	Registered (12-May- 2016)	N	73178	SECURITY SEED AND CHEMICAL, INC	1	Chitosan

# **Summary Report**

Registration #	Name	Status	Restricted Use Product	Company #	Company Name	Percent Active Ingredient	Active Ingredient
1381-256	ZURANCE	Registered (13-Feb-2015)	N	1381	WINFIELD SOLUTIONS, LLC	.18	Complex Polymeric Polyhyroxy Acid (CPPA)
33270-37	OPTIFY	Registered (09-Dec- 2014)	N	33270	WINFIELD SOLUTIONS, LLC	.18	Complex Polymeric Polyhyroxy Acid (CPPA)
33270-40	OPTIFY/STRETCH	Registered (15-Apr-2015)	N	33270	WINFIELD SOLUTIONS, LLC	.11	Complex Polymeric Polyhyroxy Acid (CPPA)
33270-40	OPTIFY/STRETCH	Registered (15-Apr- 2015)	N	33270	WINFIELD SOLUTIONS, LLC	.01	Cytokinin (as kinetin)
82940-2	Elicitore	Registered (27-Mar- 2014)	N	82940	ACTAGRO, LLC	12	Humates (as derived from Leonardite)
82940-3	PM- 4300ORGANIC ACIDS	Registered (27-Mar-2014)	N	82940	ACTAGRO, LLC	18.5	Humates (as derived from Leonardite)
84846-2	CARBON POWER	Registered (09-Jul-2013)	N	84846	FBSCIENCES, INC.	.18	Complex Polymeric Polyhyroxy Acid (CPPA)
84846-3	CARBON POWER CONCENTRATE	Registered (09-Jul-2013)	N	84846	FBSCIENCES, INC.	.9	Complex Polymeric Polyhyroxy Acid (CPPA)
84846-5	ARCUS	Registered (19-Dec- 2013)	N	84846	FBSCIENCES, INC.	.9	Complex Polymeric Polyhyroxy Acid (CPPA)

, ,							
84846-8	CARBON POWER-CA	Registered (20-Aug-2014)	N	84846	FBSCIENCES, INC.	.18	Complex Polymeric Polyhyroxy Acid (CPPA)
84846-10	OPTIFY 500	Registered (09-Dec-2014)	N	84846	FBSCIENCES, INC.	.9	Complex Polymeric Polyhyroxy Acid (CPPA)
84846-12	CITROS- F WITH CARBON POWER	Registered (06-May-2015)	N	84846	FBSCIENCES, INC.	.018	Complex Polymeric Polyhyroxy Acid (CPPA)
84846-13	ARCUS FS	Registered (17-Dec-2015)	N	84846	FBSCIENCES, INC.	.9	Complex Polymeric Polyhyroxy Acid (CPPA)



# BIOPESTICIDES REGISTRATION ACTION DOCUMENT

# **Humates**

(Humic acid; Humic acids, potassium Salts; Humic acids, sodium salts; and Humates derived from Leonardite)
PC Codes: 700132, 800286, and 021818

U.S. Environmental Protection Agency Office of Pesticide Programs Biopesticides and Pollution Prevention Division

(Last updated March 13, 2014)

# **Table of Contents**

I.	EXECUTIVE SUMMARY	1
II.	ACTIVE INGREDIENT OVERVIEW	2
III.	REGULATORY BACKGROUND	2
A.	Application for Pesticide Registration	2
B.	Food Clearances/Tolerances	3
IV.	RISK ASSESSMENT	3
A.	Product Analysis Assessment (40 CFR § 158.2030)	3
B.	Human Health Assessment	
1.	Tier I Toxicology	
2.	Tier II and Tier III Toxicity Studies	
3.		
4.	1	
6. 7.	Occupational Exposure and Risk Characterization	
C.	Environmental Assessment	8
1.	Ecological Hazards	
2.		
3.	Ecological Exposure and Risk Characterization	8
4.	Endangered Species Assessment	
D.	Product Performance Data	9
V.	RISK MANAGEMENT DECISION	9
A.	Determination of Eligibility for Registration	9
B.	Regulatory Decision	10
C.	Environmental Justice	10
VI.	ACTIONS REQUIRED BY REGISTRANTS	10
A.	Reporting of Adverse Effects	11
В.	Reporting of Hypersensitivity Incidents	11

# Humates PC Codes 700132, 800286, and 021818 Biopesticides Registration Action Document

VII.	APPENDIX A. DATA REQUIREMENTS (40 CFR PART 158, SUBPART U)	12
VIII.	APPENDIX B. REFERENCES	16
IX.	GLOSSARY OF ACRONYMS AND ABBREVIATIONS	. 17

# BIOPESTICIDES REGISTRATION ACTION DOCUMENT (BRAD) TEAM

# **Branch Chief**

Linda A. Hollis, M.S.

# Product Chemistry/Human Health Effects/Nontarget Organisms

Russell Jones, PhD, Senior Scientist Sadaf Shaukat, Biologist

# **Regulatory Action Leader**

Menyon Adams, Biologist

#### I. EXECUTIVE SUMMARY

Humates derived from Leonardite are collectively a new biochemical active ingredient (hereafter referred to as humates) intended for use as a plant growth regulator (PGR) to control the vegetative growth and maturation of agricultural and greenhouse crops. Treatment of plants with humates enhances root growth, improves the uptake of nitrogen, potassium and phosphate, increases the treated plants' ability to resist plant disease, and reduces the need to add soil nutrients and fertilizers during the growing season.

Humates are naturally occurring substances formed by the biodegradation of dead organic matter, and are often associated with deposits of coal, lignite and mudstone. They are ubiquitous in the environment in soil and water, including agricultural areas where crops are grown for human and animal consumption. Commonly used to condition soil, humates are widely regarded as being beneficial to plants. From a structural perspective, humates include a complex mixture of compounds, including humic acids and their potassium and sodium salts, fulvic acids, and humins, with humic acids being the major extractable component.

In terms of their safety to humans, including infants and children, humates have been previously evaluated and well-characterized by the U.S. Environmental Protection Agency (EPA or Agency). They are also listed among those substances that are exempt from the requirement of a tolerance under section 408 of the Federal Food, Drug, and Cosmetic Act (FFDCA) as either inert or active ingredients in a pesticide formulation when used in accordance with good agricultural and/or manufacturing practices (40 CFR Part180.950 (e)).

BPPD has reviewed all of the data and other information submitted in support of the registration of humates as a PGR under Section 3(c)(5) of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), and has determined that the current data requirements (40 CFR part 158.2010 through 158.2070) for registration of a biochemical pesticide have been satisfied. Given that humates are of very low toxicity and present little, if any, risks to humans and the environment, EPA has concluded that it is in the best interest of the public to issue registrations for the manufacturing-use product (MP), PM-4300 Organic Acids (EPA File Symbol No. 82940-G) and the end-use product (EP), Phocon (EPA File Symbol No. 82940-E), which contain humates as the active ingredient. The basis for this decision is described in more detail in section IV of this draft Biopesticide Registration Action Document (BRAD).

On October 1, 2009, EPA announced a policy to provide a more meaningful opportunity for the public to participate in major registration decisions before they occur. According to this policy, EPA provides a public comment period prior to making a registration decision for the following types of applications: new active ingredients; first food uses; first outdoor uses; first residential uses; or any other registration actions for which EPA believes there may be significant public interest.

Consistent with the policy of making registration decisions more transparent, humates are subject to a 15 day comment period as a "new active ingredient." The notice for this comment period includes the draft BRAD and draft labels for two products (PM-4300 Organic Acids (EPA File

Symbol 82940-G) and Phocon (EPA File Symbol 82940-E)) that contain this new active ingredient. The docket identification (ID) number is EPA-HQ-OPP-2012-0251. For definitions of scientific terms, please refer to <a href="http://www.epa.gov/pesticides/glossarv/">http://www.epa.gov/pesticides/glossarv/</a>.

#### II. ACTIVE INGREDIENT OVERVIEW

**Common Name:** N/A

**Chemical Names:** Humates

Humic Acids, Potassium Salts Humic Acids, Sodium Salts Humates derived form Leonardite

**Trade & Other Names:** N/A

**CAS Registry Number:** N/A

**OPP Pesticide Chemical Code:** 700132

800286 021818

**Type of Pesticide:** Biochemical Pesticide – Plant Growth Regulator

#### **Biochemical Classification**

On February 12, 2009, the Biochemical Classification Committee classified humates as a biochemical active ingredient, based upon the nontoxic mode of action as a PGR, natural occurrence in the environment, and history of human and animal exposure to humates with no toxic or other adverse effects.

For more information regarding product chemistry data requirements, please refer to Tables 1, 2, and 3 in Appendix A of this document.

#### III. REGULATORY BACKGROUND

#### A. Application for Pesticide Registration

On December 16, 2011, Ann Tillman of Pyxis regulatory Consulting, Inc., on behalf of Actagro LLC., 4110 136<sup>th</sup> St. NW, Gig Harbor, WA 98332, submitted applications to register an MP, "PM-4300 Organic Acids" (EPA File Symbol No. 82940-G), and an EP, "Phocon" (EPA File Symbol No. 82940-E), containing the new biochemical active ingredient, humates, at 18.5% and 12.0%, respectively. A notice of receipt (NOR) of the applications was published in the Federal Register on June 27, 2012, (77 FR 38285). No comments were received during the 30-day comment period following publication of the NOR.

#### **B.** Food Clearances/Tolerances

Residues resulting from the use of humates (humic acid; humic acids, potassium salts; humic acids, sodium salts) as either an inert or an active ingredient in a pesticide chemical formulation, including antimicrobial pesticide chemicals, are exempt from the requirement of a tolerance under FFDCA section 408, if such use is in accordance with good agricultural or manufacturing practices (40 CFR part 180.950 (e)). (Ref.1)

#### IV. RISK ASSESSMENT

### A. Product Analysis Assessment (40 CFR § 158.2030)

Biochemical pesticide product analysis data requirements include product chemistry and composition, analysis and certified limits, and physical and chemical characteristics. Product chemistry and composition data include information about the identity of the active ingredient, the manufacturing process, and discussion of the potential for formation of unintentional ingredients. Analysis and certified limits data include information on analysis of samples and certification of the upper and lower limits for the ingredients in a formulated product. Physical and chemical characteristics data describe basic characteristics of the registered pesticide products, including color, physical state, odor, stability, miscibility, pH, corrosion characteristics, viscosity and density.

EPA's Office of Pesticide Programs (OPP) has assigned unique pesticide chemical (PC) codes to humic acid, humic acids, potassium salts, and humic acids, sodium salts (700132, 800286 and 021818, respectively), and all of the product analysis data required for an unconditional registration have been fulfilled. (See Tables 1 and 2 in <u>Appendix A</u> of this document for a summary of product chemistry and composition, analysis and certified limits, physical and chemical characteristics data.)

### **B.** Human Health Assessment

#### 1. Tier I Toxicology

All of the toxicology data requirements have been satisfied and support the proposed registration of humates as a biochemical PGR. The data and other information submitted are summarized below (see also Tables 3 and 4 in Appendix A of this document).

a. <u>Acute Toxicity</u> (OCSPP Guideline Nos. 870.1100, 870.1200, 870.1300, 870.2400, 870.2500, and 870.2600; Master Record Identification (MRID) Nos. 48711105, 48711106,48711107, 48711108, 48711109, 48711110, 49080301, 48711115):

Acute toxicity testing of a pesticide active ingredient and/or product is required to: 1) determine systemic toxicity from acute exposure via the dermal, inhalation and oral routes; 2) determine irritant effects from exposure to the eyes and skin; and 3) determine the potential for skin sensitization (allergic contact dermatitis). Acute Toxicity Categories I, II, III, or IV (Toxicity Category I indicates the highest toxicity, and Toxicity Category IV is the lowest) are assigned to

an active ingredient and EPs containing that active ingredient, and are based on the hazard(s) identified from studies and/or other information submitted to support an application to register a pesticide in the U.S.

In an acute oral toxicity test in rats, the  $LD_{50}$  for a single dose of humic acids was >11,500 mg/kg (EAEMP, 1999). Further, the results from the Tier I acute testing on the MP classify humates in Toxicity Category IV for the dermal, oral, and inhalation routes of exposure, based on the doses tested in laboratory rats. In addition, minimal eye irritation cleared in less than 24 hours and slight dermal irritation resolved within 72 hours in rats, and humates were not dermal sensitizers in guinea pigs. (For the results of these studies (i.e.,  $LD_{50}$ ,  $LC_{50}$ ), refer to Table 3 in <u>Appendix A</u> of this document.)

b. <u>Subchronic Toxicity, Developmental Toxicity, and Mutagenicity</u> (OCSPP Guideline Nos. 870.3100, 870.3250, 870.3465; 870.3700, 870.5100, 870.5300, 870.5375; MRID Nos. 48975101, 48975102):

The data submitted to fulfill the requirement for a Bacterial Reverse Mutation Test (OCSPP 870.5100) demonstrated that humates did not cause base pair changes or frame shift mutations, and there was no evidence of cytotoxicity at highest dose tested.

In lieu of conducting guideline studies, rationales were submitted to address the following: 90-Day Oral (OCSPP 870.3100), 90-Day Dermal (OCSPP 870.3250), 90-Day Inhalation (OCSPP 870-3465) and Prenatal Development (OCSPP 870.3700) toxicity studies, and the *in vitro* Mammalian Cell Assay (OCSPP 870.5300/5375). BPPD determined that the rationales are acceptable, based on the results of the studies conducted with humates as the test substance and its presence as a natural component of soil and water with no known adverse effects to humans and the environment.

# 2. Tier II and Tier III Toxicity Studies

Tier II and Tier III toxicity testing was not required due to humates' low toxicity and the low levels of human exposure expected from its intended use as a PGR.

#### 3. Endocrine Disruptors

As required by the Administrator under the Federal Food, Drug, and Cosmetic Act (FFDCA) section 408(p), the EPA has developed the Endocrine Disruptor Screening Program (EDSP) and has begun to implement the screening program that is to be used to test all pesticides in order to determine whether certain substances (including pesticide active and other ingredients) may have an effect in humans or wildlife similar to an effect produced by a "naturally occurring estrogen, or other such endocrine effects as the Administrator may designate." FFDCA section 408(p)(4) authorizes the Administrator, by order, to exempt from the requirements of the Estrogenic Substances Screening Program a biologic substance or other substance if a determination is made that the substance is not anticipated to produce any effect in humans similar to an effect produced by a naturally occurring estrogenic substance. Between October 2009 and February 2010, the EPA issued test orders/data call-ins for the first group of 67 chemicals, which contains

58 pesticide active ingredients and 9 inert ingredients. A second list of chemicals identified for screening under the EDSP was published on June 14, 2013, and includes some pesticides scheduled for registration review and chemicals found in water. Humates are not among the group of pesticide active ingredients on the lists to be screened under the EDSP.

The Agency believes that humates would not likely produce any effect in humans similar to an effect produced by a naturally occurring estrogenic substance. As such, and pursuant to Section 408(p)(4), EPA will determine in the future whether it can exempt humates from the requirements of the Section 408(p) EDSP. In the event the EPA does determine to exempt this substance from the EDSP, an order will be issued.

For further information on the status of the EDSP, the policies and procedures, the lists of chemicals, future lists, the test guidelines, and the Tier 1 screening battery, please visit our website at <a href="http://www.epa.gov/endo/">http://www.epa.gov/endo/</a>.

### 4. Dose-Response Assessment

No toxicological endpoints were identified for humates; therefore, a dose-response assessment was not required.

#### 5. Federal Food, Drug, and Cosmetic Act (FFDCA) Considerations

Section 408(c)(2)(A)(i) of FFDCA allows EPA to establish an exemption from the requirement for a tolerance (the legal limit for a pesticide chemical residue in or on a food) only if EPA determines that the exemption is "safe." Section 408(c)(2)(A)(ii) of FFDCA defines "safe" to mean that "there is a reasonable certainty that no harm will result from aggregate exposure to the pesticide chemical residue, including all anticipated dietary exposures and all other exposures for which there is reliable information." This includes exposure through drinking water and in residential settings but does not include occupational exposure. Pursuant to section 408(c)(2)(B) of FFDCA, in establishing or maintaining in effect an exemption from the requirement of a tolerance, EPA must take into account the factors set forth in section 408(b)(2)(C) of FFDCA, which require EPA to give special consideration to exposure of infants and children to the pesticide chemical residue in establishing a tolerance exemption and to "ensure that there is a reasonable certainty that no harm will result to infants and children from aggregate exposure to the pesticide chemical residue...." Additionally, section 408(b)(2)(D) of FFDCA requires that EPA consider "available information concerning the cumulative effects of [a particular pesticide's]... residues and other substances that have a common mechanism of toxicity."

EPA performs a number of analyses to determine the risks from aggregate exposure to pesticide residues. First, EPA determines the toxicity of pesticides. Second, EPA examines exposure to the pesticide through food, drinking water, and other routes as a result of pesticide use in residential settings.

Consistent with section 408(b)(2)(D) of FFDCA, EPA reviewed the available scientific data and other relevant information, and considered its validity, completeness, and reliability, and the relationship of this information to human risk. EPA also considered available information concerning the variability of the sensitivities of major identifiable subgroups of consumers,

including infants and children. Based on the acute toxicity data and information discussed previously and presented in Table 3 in <u>Appendix A</u> of this document, the data requirements for a human health dietary risk assessment for humates have been fulfilled.

## a. Aggregate Exposure

In examining aggregate exposure, section 408 of FFDCA directs EPA to consider available information concerning exposures from the pesticide residue in food and all other non-occupational exposures, including drinking water from ground or surface water, pesticide use in gardens, residential and other lawns and landscapes, and buildings (residential and other indoor uses). EPA expects the aggregate exposure to residues of humates from the PGR use to be negligible when compared to the ordinary, everyday levels to which individuals are already exposed in the natural environment, since humates are commonly found in soil and water. The aggregate exposure potential for humates is discussed below.

<u>Food Exposure and Risk Characterization</u>: Since humates are common components of agricultural soil, EPA expects that human dietary exposure to residues of humates resulting from its pesticidal uses would be negligible in comparison to naturally occurring humates. Further, residues of humates from use as a PGR would be very low, since they are not absorbed by plants, and rainfall and irrigation would reduce the amount of applied product during the growing season. In the unlikely event that any residues of the pesticide remain in or on consumed food, no adverse effects would be expected, based on the lack of toxicity demonstrated in the submitted studies and other information described previously and presented in Table 3 in <u>Appendix A</u> of this document.

<u>Drinking Water Exposure and Risk Characterization</u>: According to the directions for use on the EP label, humates are not to be applied directly to bodies of water. It is possible, however, that some residues may reach bodies of water via runoff or spray drift. Since humates are common components of water, EPA expects that human exposure to residues of humates in drinking water resulting from its use as a PGR would be negligible in comparison to naturally occurring humates. In the unlikely event that any residues of the pesticide remain in drinking water, no adverse effects would be expected, based on the lack of toxicity demonstrated in the submitted studies and other information described previously and presented in Table 3 in Appendix A of this document.

<u>Non-occupational, Residential Exposure and Risk Characterization:</u> The PGR use of this active ingredient is intended only for agricultural environments, so non-occupational and residential exposures are expected to be minimal to non-existent. Should exposure occur, the risks to humans is expected to below level of concern, based upon the low toxicity of humates demonstrated in the data and other information submitted and evaluated by the EPA. (Ref. 1; see also <u>Section IV.B.1.a</u> of this BRAD).

#### b. Cumulative Effects from Substances with a Common Mechanism of Toxicity.

Section 408(b)(2)(D)(v) of FFDCA requires that, when considering whether to establish, modify, or revoke a tolerance exemption, EPA consider "available information concerning the

cumulative effects of [a particular pesticide's] . . . residues and other substances that have a common mechanism of toxicity."

Humates are not known to have a common mechanism of toxicity with other substances; therefore, cumulative effects with other substances are not anticipated. For information regarding EPA's efforts to identify chemicals that may have a common mechanism of toxicity and to evaluate the cumulative effects of such chemicals, see EPA's website at <a href="http://www.epa.gov/pesticides/cumulative">http://www.epa.gov/pesticides/cumulative</a>.

#### c. Determination of Safety for the U.S. Population, Infants and Children

Based on its analyses of the submitted toxicity data (refer to Section IV.B.1. a and Table 3 in Appendix A), EPA concludes that there are no threshold effects of concern to infants, children, or adults when PGR products containing humates as an active ingredient are used as labeled in accordance with good agricultural practices. No toxicological effects or endpoints were identified in mammalian studies. The Agency does not expect that infants and children will have special sensitivity to residues of humates. As a result, no additional margin of exposure (safety) is necessary to protect infants and children and that not adding an additional margin of exposure (safety) will be safe for infants and children.

The Agency also concludes that there is a reasonable certainty that no harm will result to the U.S. population, including infants and children, from aggregate exposure to the residues of humates when used as labeled and in accordance with good agricultural practices as a PGR. Such exposure includes all anticipated dietary exposures and all other exposures for which there is reliable information. EPA arrived at this conclusion because, considered collectively, the data available on humates do not demonstrate toxic potential to humans, including infants and children

## 6. Occupational Exposure and Risk Characterization

An occupational exposure assessment was not conducted and is not required for biochemical pesticides (40 CFR part 158.2010). Appropriate personal protective equipment (PPE) requirements on the label will mitigate any unintentional exposures to applicators and/or handlers.

#### 7. Human Health Risk Characterization

EPA considered human exposure to humates in light of the standard for registration in FIFRA and the relevant safety factors in FFDCA. Since there were no toxicological effects or endpoints identified in mammalian studies, a determination has been made that no unreasonable adverse effects to the U.S. population in general, and to infants and children in particular, will result when humate products are used in accordance with EPA-approved labeling.

#### C. Environmental Assessment

# 1. Ecological Hazards

Adequate nontarget toxicology data/information submitted and reviewed by the Agency satisfies the non-target toxicology data requirements for humates.

Avian Oral Acute Toxicity, Avian Dietary Toxicity, Fish Acute Toxicity, Freshwater and Marine, and Aquatic Invertebrate Acute Toxicity (OCSPP Guideline Nos. 850.2100, 850.2200,850.1075, and 850.1010) (see also Tables 5 and 6 in Appendix A of this document).

Humates have historically been applied to soil with no reports of adverse effects to humans, other mammals, or the environment. Since humates are ubiquitous in soil and water, birds, fish, and other living organisms are already naturally exposed. The data and other information submitted to support the registration of humates as a PGR demonstrate that humates are practically nontoxic to birds on a dietary basis ( $LC_{50} > 5620$  ppm), practically nontoxic to fish ( $LC_{50} > 100$ mg/L), and practically nontoxic to aquatic invertebrates ( $EC_{50} > 100$ mg/L).

# Seedling Emergence and Vegetative Vigor (OCSPP Guidelines Nos. 850.4100 and 850.4150)

Humates are intended to be applied to growing crops, and are not absorbed by plants when applied to crops or to soil near growing crops. The major component, humic acids, enriches the soil and stimulates root growth and uptake of nutrients by the treated plants. They have historically been applied to crops with no reports of adverse effects to the environment. Humates provide benefits to soils and plants, and are considered to have a nontoxic mode of action.

# Non-target Insect Testing (OCSPP Guideline 880.4350)

Humates are intended to be formulated into EP's and intended for application to growing crops. There have been no reports in the public literature of deleterious effects to honey bees from exposures to humic acid or other humic substances.

#### 2. Environmental Fate and Ground Water Data

Environmental fate and groundwater data are not required at this time because the results of the nontarget organism toxicity assessment (Tier I data requirements) did not trigger these Tier II data requirements.

#### 3. Ecological Exposure and Risk Characterization

Humates are naturally occurring and ubiquitous in both soil and aquatic environments. The proposed EP label rates would result in little net increase in the background amount of humates already present in the environment. Based on the review of this body of information in conjunction with the proposed labeling, the Agency believes that when used in accordance with the label directions, the use of humates should not result in adverse effects to birds, fish, aquatic invertebrates, and plant or nontarget insects. (Ref. 1)

#### 4. Endangered Species Assessment

EPA has determined that no adverse effects are anticipated for nontarget species exposed to humates when used as a PGR; therefore, effects to federally-listed threatened and endangered species and their designated critical habitats are also not expected. Therefore, a "No Effect" determination is made for direct and indirect effects to federally-listed endangered and threatened species and their designated critical habitats for the proposed uses of humates as a PGR in agricultural settings.

#### D. Product Performance Data

Product performance (efficacy) data must be developed for all pesticides to ensure that the products will perform as intended and that unnecessary pesticide exposure to the environment will not occur as a result of the use of ineffective products. The Agency reserves the right to require, on a case-by- case basis, the submission of efficacy data for any pesticide product registered or proposed for registration, but applications to register pesticide products intended to control a pest of significant public health importance, as defined in FIFRA section 28(d) and section 2(nn), must include such data. For further guidance on the product performance data requirement, refer to Pesticide Registration (PR) Notices 96-7, 2002-1 and Explanation of Statutory Framework for Risk-Benefit Balancing for Public Health Pesticides (http://www.epa.gov/PR\_Notices/pr1996-7.pdf, http://www.ea.gov/PR\_Notices/pr2002-1.pdf, and http://www.epa.gov/pesticides/health/risk-benefit.htm).

Humates are not intended to be formulated into products to control public health pests, and product performance was not evaluated by the Agency.

#### V. RISK MANAGEMENT DECISION

#### A. Determination of Eligibility for Registration

Section 3(c)(5) of FIFRA provides for the registration of a pesticide provided that all the following determinations are made: (1) its composition is such as to warrant the claims for it; (2) its labeling and other materials required to be submitted comply with the requirements of FIFRA; (3) it will perform its intended function without unreasonable adverse effects on the environment; and (4) when used in accordance with widespread and commonly recognized practice, it will not generally cause unreasonable adverse effects on the environment.

To satisfy criterion (1), EPA believes the composition the proposed MP and EP warrants the claims made on the labels. Criterion (2) is satisfied, since the proposed product labels, as well as the data and information presented in this document, are in compliance with the requirements of FIFRA. Criterion (3) is satisfied in that humates are expected to function as PGRs without causing unreasonable adverse effects on the environment. Criterion (4) is satisfied in that no unreasonable adverse effects are expected when products containing humates are used in accordance with label directions and commonly recognized agricultural practices. Therefore, PM-4300 Organic Acids (EPA File Symbol No. 82940-G), and Phocon (EPA File Symbol No.

82940-E) meet the requirements for registration under FIFRA section 3(c)(5) for use in agricultural settings.

#### **B.** Regulatory Decision

The data submitted fulfill the requirements for the unconditional registration of humates for use as a plant growth regulator. For product-specific information, please refer to <a href="http://www.epa.gov/pesticides/pestlabels">http://www.epa.gov/pesticides/pestlabels</a>.

#### C. Environmental Justice

For additional information regarding environmental justice issues, please visit EPA's website at <a href="http://www.epa.gov/compliance/environmentaljustice/index.html">http://www.epa.gov/compliance/environmentaljustice/index.html</a>.

EPA seeks to achieve environmental justice—the fair treatment and meaningful involvement of all people regardless of race, color, national origin, or income—with respect to the development, implementation, and enforcement of environmental laws, regulations, and policies. Fair treatment means that no group of people, including racial, ethnic, or socioeconomic groups, should bear a disproportionate share of the negative environmental consequences resulting from industrial, municipal, and commercial operations or the execution of federal, state, local, and tribal environmental programs and policies. Meaningful involvement means that (1) potentially affected community residents have an appropriate opportunity to participate in decisions about an activity that will affect their environment and/or health; (2) the public's contribution can influence the regulatory agency's decision; (3) the concerns of all participants involved will be considered in the decision-making process; and (4) the decision-makers seek out and facilitate the involvement of those potentially affected. EPA has this goal for all communities and persons across the U.S.

At this time, EPA does not believe that use of humates pesticide products will cause harm or a disproportionate impact on at-risk communities; however, please comment if you are aware of any groups or segments of the population who, as a result their location, cultural practices, or other factors, may have atypical, unusually high exposure to humates compared to the general population.

For additional information regarding environmental justice issues, please visit EPA's web site at <a href="http://www.epa.gov/compliance/environmentaljustice/index.html">http://www.epa.gov/compliance/environmentaljustice/index.html</a>.

## VI. ACTIONS REQUIRED BY REGISTRANTS

EPA evaluated all data submitted in connection with the registration of the new active ingredient, humates, and determined that these data are sufficient to satisfy current registration data requirements. At this time, no additional data must be submitted to EPA for these particular products. For new uses and/or changes to existing uses, EPA may require additional data.

Notwithstanding the information stated in the previous paragraph, it should be clearly understood that before releasing the registered products for shipment, the registrant will be required to

Humates PC Codes 700132, 800286, and 021818 Biopesticides Registration Action Document

provide appropriate final printed labeling to EPA. Further, certain specific data, briefly described below, are required to be reported to EPA, as a requirement for maintaining the federal registration for all pesticide products.

# A. Reporting of Adverse Effects

Pursuant to FIFRA section 6(a)(2), reports of all incidents of adverse effects to the environment must be submitted to EPA.

# **B.** Reporting of Hypersensitivity Incidents

Under the provisions of 40 CFR part 158.2050(d), all incidents of hypersensitivity (including both suspected and confirmed incidents) must be reported to the Agency.

# VII. APPENDIX A. Data Requirements (40 CFR Part 158, Subpart U)

Master Record Identification (MRID) numbers listed in the following tables are representative of supporting data/information for the original registration of the product containing this active ingredient. Subsequent to this registration, there may be additional MRIDs that support registration of other products containing this active ingredient.

TABLE 1. Product Identi	TABLE 1. Product Identify, Composition, Analysis and Certified Limits for PM-4300 Organic Acids (40 CFR 158.2030)			
OPPTS Guideline Reference No.	Study	Results		
830.1550 to 830.1670	Product identity; Manufacturing process; Discussion of formation of unintentional ingredients	Acceptable; Confidential Business Information (CBI)		
830.1700	Analysis of samples	Acceptable; CBI		
830.1750	Certification of limits	Acceptable; CBI		
830.1800	Analytical method	Acceptable; CBI		

TABLE 2. Physical and Chemical Properties for PM-4300 Organic Acids (40 CFR 158.2030)

MRID Nos. 48711101- 48711104 and 49080300

Property/OCSPP Guideline	Description of Result	Methods
Color/ 830.6302	Black Munsell N1 1/N	Visual inspection at 21.4°C
Physical State/ 830.6303	Liquid	Visual inspection at 21.5°C
Odor/830.6304	Mild, alcoholic	Olfactory inspection at 21.5°C
Stability/830.6313	Stable for 14 days at ambient and elevated $(54 \pm 2^{\circ}\text{C})$ temperature in HDPE containers. Stability to metals and metal ions is not applicable, since the product will not be stored or packaged in metal containers.	OCSPP 830.1637
Oxidation/Reduction: Chemical Incompatibility/830.6314	Not applicable, the product does not contain oxidizing ingredients.	N/A
Flammability/830.6315	Not applicable, the product is 70% water and contains no flammable ingredients. >100°C <sup>b</sup>	N/A
Explodability/830.6316	Not applicable, the product is 70% water and contains no explosive N/A ingredients.	
Storage Stability/830.6317	Study is ongoing. Results will be submitted upon completion.	N/A
Miscibility/830.6319	Not applicable, the product is not an emulsifiable liquid to be diluted with petroleum solvents.	N/A
Corrosion Characteristics/830.6320	Study is ongoing. Results will be submitted upon completion.	N/A
Dielectric Breakdown Voltage/830.6321	Not applicable, the product is not for use around electrical equipment.	N/A
pH/830.7000	$10.67 \pm 0.005(1\% \text{ solution in CO}_2\text{-free}$ water at 21.1°C)	pH meter Maxxam SOP 91-M-014
Viscosity/830.7100	$3.01 \pm 0.00 \text{ mm}^2/\text{s (cSt)}$ at $19.8^{\circ}\text{C}$ $2.53 \pm 0.00 \text{ mm}^2/\text{s (cSt)}$ at $39.9^{\circ}\text{C}$	Ubbelohde viscometer
Melting Range/830.7200	Not applicable; the product is a liquid.	N/A
Boiling Range/830.7220	102.6 ± 0.1°C	Ebulliometric method
Density/Relative Density/Bulk Density/830.7300	$1.14 \pm 0.00 \text{ g/mL}$	OECD 109
Dissociation Constant in Water/830.7370	Not applicable, the product is 70% water.	N/A
Partition Coefficient/830.7550	Not applicable, the product is 70% water and the components are not expected to partition into octanol.	
Water Solubility/830.7840	Not applicable, the product is 70% water.	N/A
Vapor Pressure/830.7950	Not applicable, the product is 70% water and contains non-volatile solutes.	N/A

TABLE 3. Acute Toxicity Data for PM-4300 Organic Acids (40 CFR 158.2050)				
Study Type/OCSPP Guideline	<u>LD<sub>50</sub>/LC<sub>50</sub>/Results</u>	<u>Toxicity</u> <u>Category</u>	<u>MRID</u>	
Acute Oral Toxicity/870.1100	>5,000 mg/kg	IV	48711105	
Acute Dermal Toxicity/870.1200	> 5,000 mg/kg	IV	48711106	
Acute Inhalation Toxicity870.1300	>2.05 mg/L	IV	48711107	
Acute Eye Irritation/870.2400	Minimal effects clearing in less than 24 hours	IV	48711108	
Acute Dermal Irritation/870.2500	Slight irritation resolved within 72 hours	IV	48711109	
Skin Sensitization/870.2600	Not a sensitizer	N/A	48711110	
Bacterial Reverse Mutation Testing/870.5100	PM-4300 did not cause gene mutations by base pair changes or frame shifts; no evidence of cytotoxicity at highest does tested; non- mutagenic/Acceptable	N/A	49080301	
In vitro Mammalian Cell Assay/870.5300/5375	Rationale/Acceptable	N/A	48711115	
90-Day Oral Toxicity/870.3100	Rationale/Acceptable	N/A	48711115	
90-Day Dermal Toxicity/870.3250	Rationale/Acceptable	N/A	48711115	
90-Day Inhalation Toxicity/870.3465	Rationale/Acceptable	N/A	48711115	
Prenatal Development/870.3700	Rationale/Acceptable	N/A	49080301	

The request to bridge acute toxicity data produced for PM-4300 (TGAI/MP) to Phocon was acceptable.

TABLE 4. Acute Toxicity Data for Phocon (40 CFR 158.2050)				
Acute Oral Toxicity	Rationale-acceptable			
Acute Dermal Toxicity	Rationale-acceptable			
Primary Eye Irritation	Minimal irritation: IV			
Primary Dermal Irritation	Rationale-acceptable			
Dermal Sensitization	Rationale-acceptable			
Acute Inhalation Toxicity	Rationale-acceptable			

TABLE 5. Ecological Toxicity Data Requirements for PM-4300 Organic Acids (40 CFR 158.2060)			
Study Type/OCSPP Guideline	Results	MRID	
Avian Acute Oral/850.2100	Rationale/Acceptable	49080302	
Avian Dietary/850.2200	96 hour LC <sub>50</sub> > 5620ppm; Practically Nontoxic	48711112	
Freshwater Fish LC <sub>50</sub> /850.1075	96 hour LC <sub>50</sub> > 100 mg/L; Practically Nontoxic	48711113	
Freshwater Invertebrate/850.1010	48 hour EC <sub>50</sub> > 100 mg/L Practically Nontoxic	48711114	
Non-target Plants/850.4100/4150	Rationale/Acceptable	48711116	
Non-target Insects/850.3020	Rationale/Acceptable	48711116	

TABLE 6. Ecological Toxicity Data Requirements for Phocon (40 CFR 158.2060)				
Study Type/OCSPP Guideline	Results/Toxicity Category	MRID	Study Conclusion	
Avian Acute Oral/850.2100	Information submitted to justify rationale	Acceptable	49080203	
Avian Dietary/850.2200	Information submitted to justify rationale	Acceptable	48711116	
Freshwater Fish LC <sub>50</sub> /850.1075	Information submitted to justify rationale	Acceptable	48711116	
Freshwater Invertebrate/ 850.1010	Information submitted to justify rationale	Acceptable	48711116	
Non-target Plants/850.4100	Pre-emergence application at 24 qt/A did not reduce by 25% or greater any of the 21-day growth endpoints for species tested	Acceptable	48710906	
Non-target Plants/850.4150	Foliar application at 24 qt/A did not reduce by 25% or greater any of the growth endpoints for species tested at 21 days post application	Acceptable	48710907	
Non-target Insects/850.3020	48-hr contact LD <sub>50</sub> >100μg/bee; relatively nontoxic to honey bee	Acceptable	48710908 and 49080203	

#### VIII. APPENDIX B. References

- 1. U.S. EPA, 2012. Memorandum from Sadaf Shaukat to Menyon Adams. Science Review in support of the Registration of PM-4300 Organic Acids Containing 18.5% Organic Acids derived from Leonardite as its Active Ingredient. U.S. Environmental Protection Agency, Office of Pesticide Programs. December 18, 2012.
- 2. U.S. EPA, 2013. Memorandum from Sadaf Shaukat to Menyon Adams. Science Review in support of the Registration of PM-4300 Organic Acids Containing 18.5% Organic Acids derived from Leonardite as its Active Ingredient. U.S. Environmental Protection Agency, Office of Pesticide Programs. September 6, 2013.
- 3. U.S. EPA, 2012. Memorandum from Sadaf Shaukat to Menyon Adams. Science Review in support of the Registration of Phocon Containing 12.0% Organic Acids derived from Leonardite as its Active Ingredient. U.S. Environmental Protection Agency, Office of Pesticide Programs. December 22, 2012.
- 4. U.S. EPA, 2013. Memorandum from Sadaf Shaukat to Menyon Adams. Science Review in support of the Registration of Phocon Containing 12.0% Organic Acids derived from Leonardite as its Active Ingredient. U.S. Environmental Protection Agency, Office of Pesticide Programs. January 23, 2013.
- 5. U.S. EPA, 2013. Memorandum from Sadaf Shaukat to Menyon Adams. Science Review in support of the Registration of Phocon Containing 12.0% Organic Acids derived from Leonardite as its Active Ingredient. U.S. Environmental Protection Agency, Office of Pesticide Programs. September 6, 2013.
- 6. OECD. 2004. SIDS Initial Assessment Report. Gluconic Acid and its Derivatives. Paris, France.
- 7. Pena-Mendez, E. M., Havel, J., Patocka, J. 2005. J. Applied Biomedicine. 3: 13-24.
- 8. Thurman EM. 1985. Organic Geochemistry of Natural Waters. Kluwer, Boston, MA, USA.
- 9. (40 CFR §180.950 (e)).
- 10. ASA Analytics. 2010. Natural organic matter (NOM) in water. <a href="http://www.anaanalytics.com/natural-organic-matter.php">http://www.anaanalytics.com/natural-organic-matter.php</a>

#### IX. GLOSSARY OF ACRONYMS AND ABBREVIATIONS

a.i. active ingredient

BPPD Biopesticides and Pollution Prevention Division BRAD Biopesticide Registration Action Document

bw body weight

CBI Confidential Business Information CFR Code of Federal Regulations

cm<sup>3</sup> cubic centimeter

CSF Confidential Statement of Formula

°C degrees Celsius

EC<sub>50</sub> median effective concentration. A statistically derived single concentration in

environmental medium that can be expected to cause an effect in 50% of the test animals when administrated by the route indicated (inhalation). It is expressed

as a concentration in air or water (e.g. mg/L).

EDSP Endocrine Disruptor Screening Program

EDSTAC Endocrine Disruptor Screening and Testing Advisory Committee

EP end-use product

EPA Environmental Protection Agency (the "Agency")

FDA Food and Drug Administration

FFDCA Federal Food, Drug, and Cosmetic Act

FIFRA Federal Insecticide, Fungicide, and Rodenticide Act

FQPA Food Quality Protection Act

FR Federal Register

g gram ha hectare kg kilogram

Kow octanol-water partition coefficient

L liter

 $LC_{50}$  median lethal concentration. A statistically derived single concentration in air or

water that can be expected to cause death in 50% of the test animals when administrated by the route indicated (inhalation and environment). It is

expressed as a concentration in air or water (e.g. mg/L).

LD<sub>50</sub> median lethal dose. A statistically derived single dose that can be expected

to cause death in 50% of the test animals when administered by the route

indicated (oral and dermal). It is expressed as a weight of

substance per unit weight of animal (e.g., mg/kg).

MRID No. Master Record Identification Number

mg milligram mPa millipascal mL milliliter

MP manufacturing-use product

N/A not applicable NE "No Effect"

NIOSH National Institute for Occupational Safety and Health

nm nanometer

#### Humates PC Codes 700132, 800286, and 021818

#### **Biopesticides Registration Action Document**

NOEL no-observed-effect-level

NOF notice of filing NOR notice of receipt

OPP Office of Pesticide Programs

OCSPP Office of Chemical Safety and Pollution Prevention

pa pascal

PPE personal protective equipment PR Notice Pesticide Registration Notice

TGAI technical grade of the active ingredient

ug microgram

USDA United States Department of Agriculture

UV ultra-violet



# BIOPESTICIDES REGISTRATION ACTION DOCUMENT

Salicylic Acid

PC Code: 076602

U.S. Environmental Protection Agency Office of Pesticide Programs Biopesticides and Pollution Prevention Division

**January 10, 2012** 

# TABLE OF CONTENTS

I.	EXECUTIVE SUMMARY	4
II.	ACTIVE INGREDIENT OVERVIEW	5
III.	REGULATORY BACKGROUND	5
	A. Classification	5
	B. Food Clearances/Tolerances	6
IV.	RISK ASSESSMENT	6
	A. Product Analysis Assessment	7
	B. Human Health Assessment	8
	C. Environmental Assessment	15
V.	ENVIRONMENTAL JUSTICE	18
VI.	RISK MANAGEMENT AND REGISTRATION DECISIONS	18
	A. Determination of Eligibility	19
	B. Regulatory Decision	19
	C. Labeling	19
VII.	. ACTIONS REQUIRED OF THE REGISTRANT	19
	A. Reporting of Adverse Effects and Hypersensitivity Incidents	20
VII	I. GLOSSARY OF ACRONYMS AND ABBREVIATIONS	20
IX.	BIBLIOGRAPHY STUDIES SUBMITTED IN SUPPORT OF THESE	
	REGISTRATIONS	21
	A. Studies Submitted in Support of Salicylic Acid.	21
	B. EPA Risk Assessment Memoranda	28
	C References	28

# BIOPESTICIDES REGISTRATION ACTION DOCUMENT TEAM

# Office of Pesticide Programs Biopesticides and Pollution Prevention Division Biochemical Pesticides Branch (BPB)

Chris Pfeifer Regulatory Action Leader
Linda Hollis Branch Chief
Angela Gonzales Lead Science Reviewer
Russell Jones, Ph.D. Senior Biologist

#### I. EXECUTIVE SUMMARY

Salicylic Acid is a naturally occurring plant regulator present in most plants. Data indicate that it triggers immune responses in plants and acts as a mild antibiotic. Humans consume Salicylic Acid regularly as it is naturally present in most fruits and vegetables. In its concentrated state, it is a white crystalline powder with a sweetish acrid taste. It is known for its many useful ester derivatives and can be found in a range of commercial products such as antiseptics, preservatives, and medicines. Salicylic Acid is perhaps best known as the principal metabolite and component of aspirin. Humans have a long history of natural exposure to Salicylic Acid without incident.

As an active ingredient, it is intended for use as a treatment for seeds that are not meant for human or animal consumption. Its mode of action is as a Systemic Acquired Resistance (SAR) inducer for seedlings – i.e. a trigger for invoking a seedling's natural defenses against pathogens, allowing for greater plant vigor and survivability. Because there are no residues taken up systemically, and treated seeds are not allowed for food or feed uses, this seed treatment is not considered to be a food use.

Negligible dietary exposures to the pesticidal active ingredient notwithstanding, there are few apparent risks related to regular exposure to this natural acid. Data from a Dutch Food Consumption Survey show the average daily intake (ADI) for this chemical has been estimated to be 0-5 milligrams per day from the consumption of fruits and vegetables. Also, consumption of Salicylic Acid in aspirin exposes a person to greater doses than would any potential residues associated with seed treatment. (HSDB, 2008) Furthermore, Salicylic Acid is approved for use by the U.S. Food and Drug Administration (FDA) as an indirect food additive under 21 CFR 175.105; and the U.S. Environmental Protection Agency (EPA or Agency) has approved the use of the chemical as an 'other ingredient' in pesticide products. In sum, no hazards have been identified yet with regard to any of these regular exposures.

Moreover, data demonstrate that Salicylic Acid poses minimal hazards for humans and the environment. Acute human health toxicity data indicate negligible human toxicity for all routes of exposure. Acute nontarget organism toxicology data indicate marginal toxicity for aquatic organisms, birds, mammals, insects and plants. Subchronic and chronic toxicity data suggest no hazard relative to longer term exposures, although no long-term exposures to Salicylic Acid formulated as a pesticidal active ingredient are anticipated given that Salicylic Acid biodegrades rapidly. No human health or environmental risks are anticipated for Salicylic Acid due to its low toxicity and minimal opportunity for significant exposure.

On October 1, 2009, the EPA announced a new policy to provide a more meaningful opportunity for the public to participate in major registration decisions before they occur. According to this policy, EPA intends to provide a public comment period prior to making a registration decision for, at minimum, the following types of applications: new active ingredients; first food uses; first outdoor uses; first residential uses; or any other registration actions for which EPA believes there may be significant public interest.

Consistent with the policy of making registration actions more transparent, the proposed pesticide products containing Salicylic Acid, a new active ingredient, are subject to a 30-day comment period. In addition to containing a new active ingredient, the registration of these products would result in the first outdoor use for Salicylic Acid. The docket identification number associated with these registration actions, EPA-HQ-OPP-2011-0009, can be accessed through <a href="http://www.regulations.gov/">http://www.regulations.gov/</a>. The following documents are available for comment in the docket: (1) Salicylic Acid Biopesticides Registration Action Document; (2) a draft label for the Manufacturing-use Product, EPA File Symbol 34704-RNLT; and (3) draft labels for the End-use Products, EPA File Symbols 34704-RNLL and 34704-RNLA. While a final decision on registration is contingent upon review and consideration of public comments, EPA presently believes that, based upon the risk assessment and information submitted in support of Salicylic Acid, it is in the best interest of the public and the environment to issue these registrations. The basis for this preliminary decision can be found in the risk assessment for Salicylic Acid, which is presented in this document.

#### II. ACTIVE INGREDIENT OVERVIEW

**Common Name:** Salicylic Acid

Chemical Names: 2-Hydroxybenzoic acid, Carboxylic Acid

Trade & Other Names: Salicylic Acid, SA

CAS Registry Number: 69-72-7

**OPP Chemical Code:** 076602

**Type of Pesticide:** Plant Regulator

#### III. REGULATORY BACKGROUND

On February 2, 2011, EPA published in the Federal Register (76 FR 5805) a notice announcing that Loveland Products, Inc., c/o Pyxis Consulting, Inc., 4110 136th St., NW., Gig Harbor, WA 98332, submitted an application to register a Manufacturing-use Product (MP), EPA File Symbol 34704-RNLT, and two End-use Products (EPs), EPA File Symbols 34704-RNLL and 34704-RNLA, containing a new active ingredient (Salicylic Acid) not included in any currently registered products. No comments were received following publication of the notice.

#### A. CLASSIFICATION

Salicylic Acid was classified as a Biochemical Pesticide by the Classification Committee on November 20, 1997. The Classification Committee confirmed its nontoxic mode of action, its

natural occurrence in the environment, and its history of exposure to humans and the environment without known toxicity.

Salicylic Acid is a naturally occurring plant hormone present in all terrestrial plants. Historically, it has been commercially distilled from willow bark, where it is found in high concentration. With regard to its active properties, Salicylic Acid is a plant regulator that has mediating roles on plant growth, photosynthesis, transpiration, and ion uptake. When applied to seeds as an active ingredient, Salicylic Acid acts as a SAR inducer – i.e. it triggers a plants immuno-defense system to defend against pathogens, allowing for greater survivability of seedlings.

#### **B. FOOD CLEARANCES/TOLERANCES**

Salicylic Acid is intended for use as a seed treatment for nonfood and nonfeed uses (i.e. treated seeds are not for animal or human consumption). Because no residues are systemically expressed through the planted seed to the fruit and vegetables, the use of Salicylic Acid is not considered to be a food use.

#### IV. RISK ASSESSMENT

On October 26, 2007, the Agency issued a Final Rule in the Federal Register on the data requirements to support registration of biochemical and microbial pesticides, and updated the definitions for biochemical and microbial pesticides (72 FR 61002). The rule became effective on December 26, 2007. The data and information evaluated for this Biopesticides Registration Action Document (BRAD) were considered in light of these requirements.

The classifications that are found for each data submission are assigned by EPA science reviewers and are an indication of the usefulness of the information contained in the documents for risk assessment. A rating of "ACCEPTABLE" indicates the study is scientifically sound and is useful for risk assessment. A "SUPPLEMENTAL" rating indicates the data provide some information that can be useful for risk assessment. The studies may have certain aspects determined not to be scientifically acceptable ("SUPPLEMENTAL: UPGRADABLE"). If a study is rated as "SUPPLEMENTAL: UPGRADABLE," EPA always provides an indication of what is lacking or what can be provided to change the rating to "ACCEPTABLE." If there is simply a "SUPPLEMENTAL" rating, the reviewer will often state that the study is not required by the current 40 CFR Part 158. Both "ACCEPTABLE" and "SUPPLEMENTAL" studies may be used in the risk assessment process as appropriate. An "UNACCEPTABLE" rating indicates that new data need to be submitted.

For the acute toxicity data requirements, Toxicity Categories are assigned for providing the appropriate precautionary labeling statements and are based on the hazard(s) identified from studies and/or other information submitted to EPA in support of a pesticide registration. The active ingredient or a particular product is classified into Toxicity Category I, II, III, or IV, where Toxicity Category I indicates the highest toxicity and Toxicity Category IV indicates the lowest toxicity.

#### A. PRODUCT ANALYSIS ASESSMENT

# 1. Product Chemistry and Composition

Salicylic Acid (2-hydroxybenzoic acid) is an aromatic carboxylic acid that is commercially derived from the bark of the willow tree. It is a naturally occurring plant regulator with various roles regulating photosynthesis and transpiration and mediating plant defenses against pathogens (U.S. EPA. 2011b.). In purest form, it is a white crystalline powder with a sweetish acrid flavor. It is used in a variety of topical cosmetics and pharmaceutical products as a mild antibiotic (HDSB, 2011). Salicylic Acid is naturally found in significant concentrations in a wide variety of foods such as apples, plums, grapes, oranges, tomatoes, cinnamon, oregano, thyme, beer, honey and raisins (HDSB, 2011).

All product chemistry data requirements for Salicylic Acid have been satisfied. As a manufactured active ingredient, Salicylic Acid extract is indistinguishable from the plant hormone that is produced naturally in plants (MRID 47206713). The extract has a high degree of purity and contains no impurities of toxicological significance (MRID 47206713, 47760931 and 47206714). All data requirements for physical and chemical characteristics have been adequately addressed (U.S. EPA. 2011b.).

## 2. Analysis and Certification of Limits

The submitted data satisfied the requirements for Analysis and Certification of Limits. Five-batch analyses and the analytical method used to determine the purity of Salicylic Acid were examined and determined to be acceptable by the Agency. The information submitted on the analyses and certified limits are summarized in Table 1.

TABLE 1. Product Chemistry Data Requirements for Salicylic Acid Technical (40 CFR § 158.2030)			
OSCPP Guideline No.	Study	Results	MRID No.
880.1100 880.1200 880.1400	Product identity; Manufacturing process; Discussion of formation of impurities	Submitted data satisfy the requirements for product identity, manufacturing process, and discussion of formation of impurities.	47206713 47760931
830.1700	Analysis of samples	Submitted data satisfy the requirements for analysis of samples.	47206714
830.1750	Certification of limits	Limits listed in the confidential statement of formula are acceptable	47206714
830.1800	Analytical method	Acceptable.	47206714

#### 3. Physical and Chemical Characteristics

The Agency has determined that the submitted data adequately describe the physical and chemical characteristics of Salicylic Acid. See Table 2 below for details.

TABLE 2. Physical and Chemical Properties of Salicylic Acid Technical (40 CFR § 158.2030)			
OCSPP	Property	Description of Result	MRID No.
Guideline No.			
830.6302	Color	White	48225202
830.6303	Physical State	Solid crystalline powder	48225202
830.6304	Odor	Odorless	48225202
		Stable for 14 days at room temperature, degrades	48225201
	Stability to Normal and	slightly (below certified limits) after 4 days at	48225202
	Elevated Temperatures,	54°C. Data on metals were not submitted; SA is	
	Metals and Metal Ions	not stored in or expected to come into contact with	
830.6313		metal or metal ions during storage or use.	
830.6315	Flammability	Flash point: 315°F (157°C)	HSDB, 2008
830.6317	Storage Stability	In progress	48225202
830.6319	Miscibility	N/A: not an emulsifiable liquid that will be diluted	
	•	with petroleum solvents.	48225202
830.6320	Corrosion Characteristics	In progress	48225202
830.7000	рН	2.56	48225201
			48225202
830.7050	UV/Visible Light	Neutral: 231 nm ( $\varepsilon^1 = 6794$ ), 296 nm ( $\varepsilon = 3567$ )	48225201
	Absorption	Basic: 219.5 nm ( $\varepsilon$ = 7046), 296.5 nm ( $\varepsilon$ = 3535)	48225202
		Acidic: 236.5 nm ( $\varepsilon$ = 8538), 302 nm ( $\varepsilon$ = 3632)	
830.7100	Viscosity	N/A: product is a solid	48225202
830.7200	Melting Point/Range	159.3-161.5 °C	48225202
830.7220	Boiling Point/Range	N/A: SA is a solid	48225202
830.7300	Density	1.429 g/mL	48225202
830.7520	Particle Size, Fiber Length	N/A: SA is not water insoluble nor is it a fibrous	48225202
	and Diameter Distribution	substance with a diameter $\geq 0.1 \mu m$ .	
830.7550	Partition Coefficient (n-	·	48225201
830.7560	Octanol/Water)	$Log P_{ow} = 2.1$	48225202
830.7570	,		
830.7840	Water Solubility	1.71 mg/mL in water	48225201
		0.05 g/100 mL in hexane	48225202
		32.12 g/100 mL in methanol	
		16.02 g/100 mL in n-octanol	
830.7950	Vapor Pressure	114 Pa at 130°C	48225202
	•	8.2X10 <sup>-5</sup> mm Hg at 25°C	

#### **B. HUMAN HEALTH ASSESSMENT**

#### 1. Toxicological Hazard Assessment

Adequate mammalian toxicology studies were provided in support of the registration of Salicylic Acid for each data requirement. Acute toxicology data indicates that the active ingredient is virtually nontoxic to mammals, and that there are no toxicological endpoints relative to its use as a SAR-inducer in plants. Accordingly, the data submitted demonstrate that the proposed uses of Salicylic Acid pose no significant risks to human health and support a finding of reasonable certainty that no harm to the general U.S. population, including infants and children, will result from exposure to this active ingredient (U.S. EPA. 2011b; MRIDs 48225203-48225208).

Table 3. Mammalian Toxicology Data for Salicylic Acid Technical (40 CFR § 158.2050)			
Study/OCSPP Guideline No.	Results	Toxicity Description	MRID No.
Acute oral toxicity (rat) (870.1100)	$LD_{50} = 890 \text{ mg/kg}$	III	47206707
Acute dermal toxicity (rabbit) (870.1200)	LD <sub>50</sub> > 5,050 mg/kg	IV	47206711
Acute inhalation toxicity (rat) (870.1300)	$LC_{50} > 2.21 \text{ mg/L}$	IV	47206710
Primary eye irritation (rabbit) (870.2400)	Moderately irritating	III	47206706
Primary dermal irritation (rabbit) (870.2500)	Non-irritating	IV	47206709
Dermal sensitization (guinea pig) (870.2600)	Not a sensitizer	N/A	47206708
Hypersensitivity incidents (None)	Must be reported	N/A	
90-Day oral toxicity (870.3100)	Proposed products are nonfood use. Subchronic and chronic oral toxicity studies were submitted for methyl salicylate and acetylsalicylic acid, which are rapidly converted to SA and/or an SA ester in the body. Data indicate negligible toxicity. Risk to humans is not anticipated based on the lack of repeat oral exposure to SA due to the use pattern.		48225204 48225206
90-Day dermal toxicity (870.3250)	Purposeful application and prolonged exposure to the human skin is not anticipated based on the use pattern (seed treatment). Significant dermal exposure to handlers/applicators is unlikely as End-use Product (EP) labels require appropriate personal protective equipment (PPE) to mitigate dermal exposure. Risk is expected to be negligible based on the lack of anticipated exposure and dermal toxicology data.		48225204 48225206
90-Day inhalation toxicity (870.3465)	Significant repeat inhalation exposure to SA as a gas, vapor or aerosol is unlikely based on use pattern as a seed treatment and physical properties of the active ingredient in that it degrades rapidly in the environment.		48225204 48225206
Mutagenicity-bacterial reverse mutation test (modified Ames) (870.5100)	Significant human exposure is unlikely based on use pattern as a seed treatment and rapid biodegradation in the environment. The risk of mutagenicity is expected to be negligible based on the lack of anticipated exposure and mutagenicity data.		HSDB, 2011
Mutagenicity-in vitro mammalian cell assay (870.5300 and 870.5375)	Significant human exposure is unlikely based on use pattern as a seed treatment and rapid biodegradation in the environment. The risk of mutagenicity is expected to be negligible based on the lack of anticipated exposure and mutagenicity data.		48225207
Developmental toxicity (870.3700)	Significant exposure to female humans is unlikely based on use pattern as a seed treatment. Significant exposure to handlers/applicators is unlikely as EP labels require appropriate PPE to mitigate exposure. Risk is expected to be negligible based on the lack of anticipated exposure and the available developmental toxicology data.		48225205

# a. Acute Toxicity – Tier I (40 CFR § 158.2050)

<u>Acute Oral Toxicity – Rat (OCSPP Guideline 870.1100; MRID No. 47206707)</u>: An acute oral toxicity study shows that the active ingredient, Salicylic Acid, has an acute oral median lethal dose (LD<sub>50</sub>) of greater than 890 milligrams per kilogram (mg/kg) in rats. The study was found

"ACCEPTABLE," and Salicylic Acid was classified as TOXICITY CATEGORY III for this route of exposure when used as a seed treatment.

<u>Acute Dermal Toxicity – Rabbit (OCSPP Guideline 870.1200; MRID No. 47206711)</u>: An acute dermal toxicity study shows that the active ingredient, Salicylic Acid, has an LD<sub>50</sub> of greater than 5,050 mg/kg in rabbits, which is considered to be virtually nontoxic. Data substantiate the active ingredient's relative dermal nontoxicity to both occupational users and the general public. The study was found "ACCEPTABLE," and Salicylic Acid was classified as TOXICITY CATEGORY IV for this route of exposure when used as a seed treatment.

<u>Acute Inhalation Toxicity – Rat (OCSPP Guideline 870.1300; MRID No. 47206710)</u>: An acute oral inhalation study shows that the active ingredient, Salicylic Acid, has a median lethal concentration (LC<sub>50</sub>) of greater than 2.21 milligrams per liter (mg/L) in rats, which shows no significant inhalation toxicity. This was the maximum dose rate, and no toxicological effects were observed on the test subjects. The study was found "ACCEPTABLE," and Salicylic Acid was classified as TOXICITY CATEGORY IV for this route of exposure when used as a seed treatment.

<u>Primary Eye Irritation – Rabbit (OCSPP Guideline 870.2400; MRID No. 47206706)</u>: A primary eye irritation study on rabbits demonstrated Salicylic Acid to be moderately irritating to the eye; however, all iritis and conjunctivitis cleared after 24 hours. The study was found "ACCEPTABLE," and Salicylic Acid was classified as TOXICITY CATEGORY III for this route of exposure when used as a seed treatment.

<u>Primary Dermal Irritation – Rabbit (OCSPP Guideline 870.2500; MRID No. 47206709)</u>: A skin irritation study on rabbits demonstrated that Salicylic Acid was not irritating to the skin. The findings are consistent with the other dermal studies and confirm that Salicylic Acid is not toxic through this route of exposure. The study was found "ACCEPTABLE," and Salicylic Acid was classified as TOXICITY CATEGORY IV for this route of exposure when used as a seed treatment.

<u>Skin Sensitization – Guinea Pig (OCSPP Guideline 870.2600; MRID No. 47206708)</u>: Data indicate Salicylic Acid is not a dermal sensitizer. Any reported incidents, however, may cause this position to be reconsidered.

Subchronic Testing (OCSPP Guidelines 870.3100, 870.3250, and 870.3465; MRID Nos. 48225204 and 48225206): In accordance with footnotes six, seven and eight in the Biochemical Pesticides Human Health Assessment Data Requirements table in 40 CFR § 158.2050, subchronic oral, subchronic dermal and subchronic inhalation testing were not required in this case because of a lack of exposure. Nonetheless, two subchronic oral tests, two subchronic dermal tests and one subchronic inhalation study were submitted. These studies are considered "SUPPLEMENTAL." One subchronic oral test used methyl salicylate as its test substance; and the other study used acetylsalicylic acid as its test substance. Both test substances readily metabolize into Salicylic Acid and are considered applicable to this risk assessment. The subchronic oral toxicity studies confirm that Salicylic Acid is not subchronically toxic through the oral route of exposure. With regard to

subchronic dermal tests on Salicylic Acid, two studies on a Salicylic Acid test substance showed no systemic toxicity and indicated no subchronic toxicity through a dermal route of exposure. With regard to subchronic inhalation toxicity, a subchronic inhalation test on methyl salicylate was submitted in lieu of a study on Salicylic Acid. The supplemental information suggests that there is no subchronic toxicity for Salicylic Acid through an inhalation route of exposure. All this supplemental information is secondary to the determination that there is virtually no exposure to this active ingredient when it is used as a seed treatment.

Developmental Toxicity (OCSPP Guideline 870.3700; MRID No. 48225205): Developmental toxicity data are conditionally required if significant exposure to female humans is expected from the proposed product's use under widespread and commonly recognized practice. Significant exposure to females is unlikely: Salicylic Acid is to be applied in a closed system that precludes significant exposure. Exposure to handlers/applicators is negligible as applications are seasonal, and EP labels require appropriate PPE. Additionally, exposure during planting is unlikely because planting is done mechanically, users are required to wear PPE and Salicylic Acid biodegrades rapidly in the environment, further mitigating exposure (HSDB, 2011). Although risk to humans is anticipated to be negligible because significant human exposure is not anticipated, "SUPPLEMENTAL" developmental toxicity studies were submitted from the open scientific literature with MRID No. 48225205. Each study suggested that the risk for developmental toxicity was negligible. The maternal no observed effect level (NOEL) in the study was 75 mg/kg Salicylic Acid, and the lowest observed effect level (LOEL) was 150 mg/kg. These findings suggest negligible developmental toxicity relative to any potential exposures to Salicylic Acid when used as a seed treatment

Mutagenicity Testing (OCSPP Guidelines 870.5100, 870.5300, and 870.5375; MRID No. 48225207): Mutagenicity data are conditionally required to support nonfood uses if the use is likely to result in significant human exposure or if the active ingredient or its metabolites are structurally related to a known mutagen or belong to any chemical class of compounds containing a known mutagen. Significant exposure to humans is unlikely based on Salicylic Acid's use pattern as a seed treatment. Significant exposure to handlers/applicators is unlikely as EP labels require PPE to further mitigate exposure. Finally, Salicylic Acid biodegrades rapidly in the environment, further mitigating exposure (HSDB, 2008). Although risk to humans has been determined to be negligible because significant human exposure is not anticipated, "SUPPLEMENTAL" mutagenicity data were submitted. Results were negative in a modified Ames mutagenicity assay with and without metabolic activation at 1, 10, and 100 µg SA/plate using Salmonella typhimurium strains TA1535, TA1537, TA1538, and TA1536 (HSDB, 2011). Furthermore, a study from the open scientific literature was provided in which Salicylic Acid and other Salicylic Acid derivatives were tested for their capacity to induce sister chromatid exchange (SCE) and chromosomal aberrations (CA) in the bone marrow of Swiss albino male mice. There was no increased incidence of SCE in the assay, indicating that Salicylic Acid is not anticipated to be mutagenic. The information submitted was determined to be adequate to support this seed treatment use.

#### b. Acute Toxicity – Tier II and Tier III (40 CFR § 158.2050)

No Tier II and Tier III studies were required, based on a lack of acute toxicity in the Tier I studies

and a lack of exposure relative to Salicylic Acid's pre-planting use pattern as a seed treatment.

#### c. Effects on the Endocrine System

As required under Federal Food, Drug, and Cosmetic Act (FFDCA) section 408(p), EPA has developed the Endocrine Disruptor Screening Program (EDSP) to determine whether certain substances (including pesticide active and other ingredients) may have an effect in humans or wildlife similar to an effect produced by a "naturally occurring estrogen, or other such endocrine effects as the Administrator may designate." The EDSP employs a two-tiered approach to making the statutorily required determinations. Tier 1 consists of a battery of 11 screening assays to identify the potential of a chemical substance to interact with the estrogen, androgen, or thyroid (E, A, or T) hormonal systems. Chemicals that go through Tier 1 screening and are found to have the potential to interact with E, A, or T hormonal systems will proceed to the next stage of the EDSP where EPA will determine which, if any, of the Tier 2 tests are necessary based on the available data. Tier 2 testing is designed to identify any adverse endocrine-related effects caused by the substance, and establish a quantitative relationship between the dose and the E, A, or T effect.

Between October 2009 and February 2010, EPA issued test orders/data call-ins for the first group of 67 chemicals, which contains 58 pesticide active ingredients and 9 inert ingredients. This list of chemicals was selected based on the potential for human exposure through pathways such as food and water, residential activity, and certain post-application agricultural scenarios. This list should not be construed as a list of known or likely endocrine disruptors.

Salicylic Acid is not among the group of 58 pesticide active ingredients on the initial list to be screened under the EDSP. Under FFDCA section 408(p), EPA must screen all pesticide chemicals. Accordingly, EPA anticipates issuing future EDSP orders/data call-ins for all pesticide active ingredients. For further information on the status of the EDSP, the policies and procedures, the list of 67 chemicals, the test guidelines and the Tier 1 screening battery, please visit our website: <a href="http://www.epa.gov/endo/">http://www.epa.gov/endo/</a>.

#### 2. Dose Response Assessment

No toxicological endpoints were identified; therefore, a dose response assessment was not required.

#### 3. Dietary Exposure and Risk Characterization

Salicylic Acid is intended for use as a pre-planting seed treatment, and is considered to be a nonfood use. Exposure to residues of Salicylic Acid is not expected. Data indicate that Salicylic Acid is not taken up into the plant systemically, and that endogenous applications biodegrade rapidly, long before a plant might fruit. Even in the incidental event of exposure to residues, no dietary risks are anticipated. Acute, subchronic, and teratogenicity studies support Salicylic Acid's nontoxic profile. It is already present in the human diet – in all fruits and vegetables – without any known detrimental effect. Furthermore, there is no information in the public literature suggesting any health issues to either animals or plants relative to this compound. In sum, no dietary exposure

is expected; and any potential dietary exposures would not be expected to pose any quantifiable risk, due to Salicylic Acid's nontoxic profile.

#### 4. Drinking Water Exposure Risk Characterization

No residues are expected in drinking water as a result of the use of Salicylic Acid as a seed treatment. Applications of Salicylic Acid are to be made directly to seeds in a closed system. Seeds are then planted directly into the soil. Because these seeds are contained in the soil, run-off due to watering seems unlikely. Even in the incidental event of exposure to residues, no dietary risks are anticipated. Acute, subchronic, and teratogenicity studies support Salicylic Acid's nontoxic profile. It is already present in the human diet – in all fruits and vegetables – without any known detrimental effect. Furthermore, there is no information in the public literature suggesting any health issues to either animals or plants relative to this compound. Negligible residues might migrate through the soil after a rain event or watering but would not be expected to reach surface water or percolate through the soil to ground water given the rapid biodegradation of Salicylic Acid and the rapid metabolization of Salicylic Acid by soil microbes. Therefore, the Agency concludes that the use of Salicylic Acid as a pre-planting seed treatment is not expected to result in any significant drinking water exposure. Altogether, drinking water exposure is not expected to pose any quantifiable risk, due to both a lack of residues and the nontoxicity of Salicylic Acid.

# 5. Acute and Chronic Dietary Exposure and Risks for Sensitive Subpopulations, Particularly Infants and Children

Dietary exposure to humans, including infants and children, is not anticipated with regard to the pesticidal use of Salicylic Acid as a seed treatment. The application is considered a nonfood use because the residue is not expressed systemically into the plant; and the active ingredient is expected to biodegrade soon after planting. In the event that there are any residues, acute toxicity studies indicate that Salicylic Acid has negligible toxicity. It is ubiquitous in nature and present in all edible plants, and there is no history of toxicological incident involving its consumption. While no dietary exposures are expected, the Agency has determined there is a reasonable certainty of no harm to the general U.S. population, including infants and children, from exposure to this active ingredient.

# 6. Occupational, Residential, School and Day Care Exposure and Risk Characterization

Occupational exposure to Salicylic Acid is anticipated to be minimal when Salicylic Acid is used as a seed treatment. It is expected to be *de minimis* for residential, school, or day care areas. In the event of incidental exposure, health risks to humans, including infants and children, are considered negligible, given Salicylic Acid's nontoxic profile.

#### a. Occupational Exposure and Risk Characterization

An occupational exposure assessment was not conducted for Salicylic Acid. Based on the proposed use pattern and toxicity data available to the Agency, there are no exposure scenarios

likely to result in unreasonable risk to humans. With regard to risks to incidental exposure, no relevant toxicological endpoints were identified.

The rationale follows: Seeds are treated in a closed system; and then seeds are incorporated directly into the soil. Pre-planting seed treatments are infrequent and seasonal. Workers treating seeds and workers planting treated seed will have PPE. Finally, given the rapid rate of biodegradation, incidental exposures related to reentry into a newly planted area are anticipated to be negligible (U.S. EPA. 2011b.). But even in the event of occupational exposure, any health risks associated with regular exposure seem unlikely. People regularly consume Salicylic Acid in their fruits and vegetables, and apply it topically in many over-the-counter antiseptics, antibiotics and cleaners. With regard to these regular exposures, there is no history of detrimental effects. Moreover, all acute, subchronic, and developmental toxicity data submitted to support the registration applications for Salicylic Acid confirm its lack of toxicity through all routes of exposure.

## b. Residential, School, and Day Care Exposure and Risk Characterization

A residential, school and day care exposure assessment was not conducted for Salicylic Acid. Products containing Salicylic Acid will be used in an agricultural setting. Based on the use pattern, residential, school and day care exposures are unlikely. In the remote event of incidental exposure to residues, the active ingredient has a nontoxic profile for all routes of exposure and a long history of consumption without incident. Due to limited exposure scenarios and negligible toxicity hazards, no risks are expected relative to these exposure scenarios.

# 7. Aggregate Exposure from Multiple Routes Including Dermal, Oral, and Inhalation

The potential for aggregate exposure is expected to be insignificant. No exposures are anticipated in non-occupational environments. Seeds treated with Salicylic Acid are incorporated into the soil directly. It has been established that Salicylic Acid biodegrades rapidly in soil; and the residues are not taken up into the plant systemically (HDSB, 2008). (Indeed, no residues are expected to be present in the seedlings.) Given a lack of any significant non-occupational exposure, a lack of concern regarding its naturally occurring background levels, and a lack of any acute toxicological endpoints for Salicylic Acid, the aggregate exposure scenario presents no significant concerns for risk.

#### 8. Cumulative Effects

Pursuant to FFDCA section 408(b)(2)(D)(v), EPA has considered available information concerning the cumulative effects of Salicylic Acid residues and other substances that have a common mechanism of toxicity. These considerations include the potential for cumulative effects on infants and children of Salicylic Acid residues and other substances with a common mechanism of toxicity. Because Salicylic Acid has a long history of dietary consumption without incident, and because no toxicological endpoints have been established, the Agency concludes that Salicylic

Acid does not share a common mechanism of toxicity, and that there are no potential cumulative effects arising from incidental exposures to Salicylic Acid residues in or on food commodities.

#### 9. Risk Characterization

The Agency considered human exposure to Salicylic Acid in light of the standard for registration in the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the relevant safety factors in FFDCA. A determination has been made that no unreasonable adverse effects to the U.S. population in general, and to infants and children in particular, will result from the use of Salicylic Acid when label instructions are followed.

#### C. ENVIRONMENTAL ASSESSMENT

1. Ecological Hazards (Relative to the Biochemical Pesticides Nontarget Organisms and Environmental Fate Data Requirements - 40 CFR § 158.2060)

Adequate nontarget toxicology data/information are available to support registration of Salicylic Acid. All nontarget toxicology data requirements for Salicylic Acid have been satisfied. There are no concerns for any nontarget organisms when Salicylic Acid is applied as a seed treatment. No toxic endpoints have been identified for nontarget mammals, nontarget birds, nontarget aquatic organisms and nontarget insects.

TABLE 4. Nontarget Organism Toxicity Requirements for Salicylic Acid Technical (40 CFR § 158.2060)  Study/OCSPP Guideline No. Results Toxicity M			MRID
Study/OCSFF Guidenne No.	Results	Category/Description	No.
Avian acute oral toxicity			
Colinus virginianus (850.2100)	$LD_{50} = 494 \text{ mg/kg}$ (95% confidence interval = 396-614 mg/kg)	Moderately toxic	47206704
Avian dietary toxicity  Colinus virginianus and Anas platyrhynchos (850.2200)	$LC_{50} > 5,000 \text{ ppm}$ NOAEL = 2,500  ppm (for both species)	Practically nontoxic	47206702 47229501
Aquatic invertebrate acute toxicity (Daphnia magna) (850.1010)	48-hour EC <sub>50</sub> = 184.88 mg/L (95% confidence interval = 182.1-187.7 mg/L)	Practically nontoxic	47206703
Freshwater fish LC <sub>50</sub> (Oncorhynchus mykiss) (850.1075)	96-hour LC <sub>50</sub> = 134.8 mg/L (95% confidence interval = 125-145 mg/L)	Practically nontoxic	47206705
Nontarget plant studies-seedling emergence (850.4100)	Based on the proposed use pattern (SA is directly applied to target seeds only prior to planting) and that SA biodegrades rapidly in the environment, seedling emergence in nontarget plants is not anticipated to be adversely impacted.		48225210
Nontarget plant studies-vegetative vigor (850.4150)	The proposed use of SA a seed treatment is not expected to result in adverse effects to vegetative vigor, as the active ingredient will not be used on seedlings or mature plants. SA is directly applied to target seeds only prior to planting.  Additionally, the active ingredient biodegrades quickly in the environment, which further precludes exposure to nontarget plants.		48225211
Nontarget insect testing ( <i>Apis mellifera</i> ) (880.4350)	96-hour acute contact $LD_{50} > 100 \mu g/bee$	Practically nontoxic	48225212

Avian Testing (OCSPP Guidelines 850.2100 and 850.2200; MRID Nos. 47206704 and 47206702): No avian toxicity is expected with regard to the pesticidal use of Salicylic Acid. Two acute oral toxicity studies were found "ACCEPTABLE." The studies established the following thresholds:  $LD_{50} = 494 \text{ mg/kg}$ , an  $LC_{50} > 5,000 \text{ ppm}$ , and an NOAEL = 2,500 ppm. Each threshold is far in excess of any anticipated exposure; and no toxicological endpoints were established. The data indicate that Salicylic Acid is practically nontoxic to birds.

Aquatic Organism Testing (OCSPP Guidelines 850.1010 and 850.1075; MRID Nos. 47206703 and 47206705): No risks are expected with regard to the exposure of aquatic organisms to Salicylic Acid. Aquatic exposure is unlikely because seed treatments are conducted in closed systems, treated seeds are incorporated directly into soil, and Salicylic Acid is known to rapidly biodegrade in soil. In the event of any aquatic exposures, the data indicate that Salicylic Acid is practically nontoxic to aquatic organisms. A nontarget aquatic invertebrate study and a freshwater fish study were found "ACCEPTABLE." The studies established the following thresholds:  $LC_{50} = 134.8$  mg/L and an  $EC_{50} > 184.88$  mg/L. Each threshold is far in excess of any anticipated exposure; and no toxicological endpoints were established. The data indicate that Salicylic Acid is practically nontoxic to aquatic nontarget organisms.

Nontarget Plant Testing (OCSPP Guidelines 850.4100 and 850.4150; MRID Nos. 4825210 and 4825211): Two nontarget plant studies were conducted. In one study, a solution containing 0.039% Salicylic Acid (the maximum dose for the proposed EP) was tested for effects on seedling emergence in ten species of plants for 21 days, during which time seedling emergence and plant height were observed. Based on the findings, there were no attributable effects to seedling emergence on nontarget plants. In the second study, a solution containing 0.039% Salicylic Acid (the maximum dose for the proposed EP) was tested for effects on vegetative vigor in ten species of plants for 21 days, during which time plant survival, growth and condition were observed. There were no reported adverse effects (25% or greater) in nine of the ten species tested when compared to controls. A statistically significant (p < 0.05) reduction of 25% was reported for the mean dry weight of ryegrass. Phytotoxic effects such as chlorosis, insect damage, leaf curl, necrosis and wilt were noted on some plants but were infrequent, generally not severe and present in both treatment and control groups. Although some phytotoxic effects were noted in this study, the proposed use of Salicylic Acid as a seed treatment is not expected to result in adverse effects to vegetative vigor, as the active ingredient will not be used on seedlings or mature plants. Moreover, the active ingredient biodegrades quickly in the environment, which further precludes exposure to nontarget plants. No toxic effects are anticipated to nontarget plants when Salicylic Acid is applied as a seed treatment.

Nontarget Insect Testing (OCSPP Guidelines 880.4350; MRID No. 48225212): An acute contact toxicity test was conducted to evaluate the toxicity to the honey bee from exposure to Salycylic Acid. Groups of young adult honey bees (Apis mellifera) were dosed topically with the active ingredient at 100, 50, 25, 12.5 and 6.25  $\mu$ g/bee. Bees were observed for mortality and other toxic effects twice within the four hours post-treatment and at 24, 48, 72 and 96 hours. Based on the observed effects, the NOEC was determined to be 25  $\mu$ g/bee and the 96-hour acute contact LD<sub>50</sub> > 100  $\mu$ g/bee. No such exposures are anticipated for nontarget insects. Nevertheless, the findings indicate that Salicylic Acid is practically nontoxic to nontarget insects.

#### 2. Environmental Fate and Ground Water Data

Environmental fate and groundwater data are not required at this time because the results of the nontarget organism toxicity assessment (Tier I data requirements) did not trigger these Tier II data requirements.

#### 3. Ecological Exposure and Risk Characterization

No significant exposure to nontarget organisms is anticipated when Salicylic Acid is applied as a seed treatment. Treatment occurs in a closed environment; and treated seeds are incorporated directly into the soil. Additionally, the active ingredient biodegrades rapidly in the environment, further precluding exposure. Regardless, the risk to nontargets is minimal. Salicylic Acid is practically nontoxic to fish, birds, mammals, aquatic invertebrates and insects. While some phytotoxicity was observed in one species of plant (of the ten tested), the effects were minimal and not attributable to Salicylic Acid.

The Agency was able to quantify the risk to terrestrial nontarget organisms through modeling. Using the Agency's Terrestrial Residue Exposure model (T-REX) version 1.4.1, risk quotients (RQs) were calculated to assess potential risk to birds. The risk quotients that were conservatively calculated using the hazard data and estimated dietary exposure (calculated using T-REX) were determined to be significantly less than the Agency's level of concern (LOC) of 0.1 for threatened and endangered avian species. This information is summarized in Table 5 below. Anticipated exposures are unlikely to result in unreasonable risk to avian species when Salicylic Acid is used as a seed treatment.

TABL	TABLE 5. Determination of Avian Risk Quotients (RQs) for Salicylic Acid Technical				
Species	LD <sub>50</sub> /NOEL	Acute RQ	Crops		
		([mg/kg bw-day]/LD <sub>50</sub> )			
Colinus virginian	$LD_{50} = 494 \text{ mg/kg}$ (95% confidence interval = 396-614 mg/kg)	0.03 (for all crops)	Barley, beans, dried beans, lima beans, snap beans, canola, corn, cotton, oats, onion, blackeyed peas, pea, lupine, grain lupine, field peas, peanuts, rice, rye, safflower, sorghum, soybeans, soybeans (edible), sugar beets, triticale, wheat.		

#### 4. Threatened and Endangered Species Assessment

The Agency has not conducted a risk assessment that supports a complete endangered species determination. The ecological risk assessment planned during registration review will allow the Agency to determine whether Salicylic Acid's use has "no effect" or "may effect" federally listed threatened or endangered species (listed species) or their designated critical habitats. When an assessment concludes that a pesticide's use "may affect" a listed species or its designated critical habitat, the Agency will consult with the U.S. Fish and Wildlife Service and/or National Marine Fisheries Services (the Services) as appropriate.

#### V. ENVIRONMENTAL JUSTICE

EPA seeks to achieve environmental justice, the fair treatment and meaningful involvement of all people, regardless of race, color, national origin, or income, in the development, implementation, and enforcement of environmental laws, regulations, and policies. To help address potential environmental justice issues, the Agency seeks information on any groups or segments of the population who, as a result of their location, cultural practices, or other factors, may have atypical, unusually high exposure to Salicylic Acid, compared to the general population. Please comment if you are aware of any sub-populations that may have atypical, unusually high exposure compared to the general population.

#### VI. RISK MANAGEMENT AND REGISTRATION DECISIONS

## A. Determination of Eligibility

Section 3(c)(5) of FIFRA provides for the registration of new active ingredients if it is determined that (A) its composition is such as to warrant the proposed claims for it; (B) its labeling and other materials required to be submitted comply with the requirements of FIFRA; (C) it will perform its intended function without unreasonable adverse effects on the environment; and (D) when used in accordance with widespread and commonly recognized practice, it will not generally cause unreasonable adverse effects on the environment.

The four criteria of the Eligibility Determination for Pesticidal Active Ingredients are satisfied by the science assessments supporting products containing Salicylic Acid. Such products are not expected to cause unreasonable adverse effects and are likely to provide protection as claimed when used according to label instructions. Therefore, EPA concludes that Salicylic Acid is eligible for registration for the labeled uses.

#### **B.** Regulatory Decision

On October 1, 2009, the EPA announced a new policy to provide a more meaningful opportunity for the public to participate in major registration decisions before they occur. According to this policy, EPA intends to provide a public comment period prior to making a registration decision for, at minimum, the following types of applications: new active ingredients; first food uses; first outdoor uses; first residential uses; or any other registration actions for which EPA believes there may be significant public interest. Accordingly, this pesticide is subject to a 30-day comment period as a new active ingredient with outdoor uses.

At this time, EPA believes, the data submitted fulfill the requirements of registration for products containing Salicylic Acid for use as a seed treatment and SAR inducer. Acute toxicity data for Salicylic Acid demonstrate that it is toxicity category III and IV for all routes of exposure. (No toxicological endpoints were established.) Data confirm that Salicylic Acid does not demonstrate subchronic or developmental toxicity, and it is not mutagenic or genotoxic. EPA has no concerns for any nontarget organisms exposed to Salicylic Acid in accordance with its approved uses. EPA has not identified any toxic endpoints for nontarget mammals, birds, plants, aquatic, or soil organisms. Nor are there any anticipated concerns for any threatened and endangered species. Given the nontoxic character of Salicylic Acid and because all applicable data requirements have been fulfilled, EPA supports its registration under FIFRA section 3(c)(5).

#### C. Labeling

Before releasing pesticide products containing Salicylic Acid for shipment, the applicant is required to provide appropriate labels.

#### VII. ACTIONS REQUIRED OF THE REGISTRANT

Biopesticides Registration Action Document

The Agency evaluated the data submitted in connection with the initial registration of Salicylic Acid and determined that these data fulfill current registration guideline requirements. No additional data are required to be submitted to the Agency at this time. Additional data may be required for new uses and/or changes to existing uses.

Page 20

Notwithstanding the information stated in the previous paragraph, it should be clearly understood that certain, specific data are required to be reported to the Agency as a requirement for maintaining the Federal registration for a pesticide product. A brief summary of these types of data are listed below.

#### A. Reporting of Adverse Effects and Hypersensitivity Incidents

Reports of all incidents of adverse effects to the environment must be submitted to the Agency under the provisions stated in FIFRA section 6(a)(2).

Additionally, all incidents of hypersensitivity (including both suspected and confirmed incidents) must be reported to the Agency under the provisions of 40 CFR § 158.2050(e).

#### VIII. GLOSSARY OF ACRONYMS AND ABBREVIATIONS

ADI	average dail	v intake

BPB Biochemical Pesticides Branch

BRAD Biopesticides Registration Action Document

CA chromosomal aberrations
CAS Chemical Abstracts Service
CFR Code of Federal Regulations

EDSP Endocrine Disruptor Screening Program

EP End-use Product

EPA United States Environmental Protection Agency (Agency)

FDA United States Food and Drug Administration

FFDCA Federal Food, Drug, and Cosmetic Act

FIFRA Federal Insecticide, Fungicide, and Rodenticide Act

FR Federal Register

g gram

g/mL gram per milliliter

Hg mercury

HSDB Hazardous Substances Data Bank

LC<sub>50</sub> median lethal concentration. A statistically derived concentration of a

substance that can be expected to cause death in 50% of test animals. It is usually expressed as the weight of substance per weight or volume of water,

air, or feed (e.g., mg/L, mg/kg, or ppm).

LD<sub>50</sub> median lethal dose. A statistically derived single dose that can be expected

to cause death in 50% of the test animals when administered by the route indicated (oral, dermal, or inhalation). It is expressed as a weight of

substance per unit weight of animal (e.g., mg/kg).

LOC level of concern

LOEL lowest observed effect level

μg microgram μm micrometer

MRID No. Master Record Identification Number

mg/kg milligram per kilogram mg/L milligram per liter mg/ml milligram per milliliter

ml milliliter mm millimeter

MP Manufacturing-use Product

nm nanometer

NOAEL no observed adverse effect level NOEC no observed effect concentration

NOEL no observed effect level

OCSPP Office of Chemical Safety and Pollution Prevention

OPP Office of Pesticide Programs

Pa pascal

PC Code Pesticide Chemical Code

ppb parts per billion

PPE personal protective equipment

ppm parts per million RQ risk quotient SA Salicylic Acid

SAR Systemic Acquired Resistance SCE sister chromatid exchange

# IX. BIBLIOGRAPHY STUDIES SUBMITTED IN SUPPORT OF THESE REGISTRATIONS

A. Studies Submitted in Support of Salicylic Acid

	States States and Stat	
MRID No.	Citation	Receipt Date
47206700	NCA Biotech, Inc. (2007) Submission of Product Chemistry and Toxicity Data in Support of the Application for Registration of Technical Salicylic Acid. Transmittal of 14 Studies.	14-Aug- 2007
47206701	Kaminsky, M. (2007) Salicylic Acid Technical: Product Chemistry: Final Report. Project Number: 10913/07. Unpublished study prepared by Stillmeadow, Inc. 14 p.	14-Aug- 2007
47206702	Gallagher, S.; Martin, K.; Beavers, J. (2006) Salicylic Acid Technical: A Dietary LC50 Study with the Mallard. Project Number: 627/102. Unpublished study prepared by Wildlife International, Ltd. 56 p.	14-Aug- 2007
47206703	Rodrigue, N. (2006) Salicylic Acid Technical: Daphnia magna 48-Hour Acute Toxicity Test: Final Report. Project Number: 9599/05. Unpublished study prepared by Stillmeadow, Inc. 12 p.	14-Aug- 2007

MRID No.	Citation	Receipt Date
47206704	Gallagher, S.; Beavers, J. (2006) Salicylic Acid Technical: An Acute Oral Toxicity Study with the Northern Bobwhite. Project Number: 627/103. Unpublished study prepared by Wildlife International, Ltd. 50 p.	14-Aug- 2007
47206705	Rodrigue, N. (2006) Salicylic Acid Technical: Rainbow Trout 96-Hour Acute Toxicity Test: Final Report. Project Number: 9600/05. Unpublished study prepared by Stillmeadow, Inc. 14 p.	14-Aug- 2007
47206706	Jia, S. (2006) Salicylic Acid Technical: Acute Eye Irritation Study in Rabbits: Amended Final Report. Project Number: 9583/05. Unpublished study prepared by Stillmeadow, Inc. 23 p.	14-Aug- 2007
47206707	Jia, S. (2006) Salicylic Acid Technical: Acute Oral Toxicity Study (UDP) in Rats: Amended Final Report. Project Number: 9580/05. Unpublished study prepared by Stillmeadow, Inc. 19 p.	14-Aug- 2007
47206708	Jia, S. (2006) Salicylic Acid Technical: Skin Sensitization Study in Guinea Pigs: Amended Final Report. Project Number: 9585/05. Unpublished study prepared by Stillmeadow, Inc. 24 p.	14-Aug- 2007
47206709	Jia, S. (2006) Salicylic Acid Technical: Acute Dermal Irritation Study in Rabbits: Amended Final Report. Project Number: 9584/05. Unpublished study prepared by Stillmeadow, Inc. 18 p.	14-Aug- 2007
47206710	Jia, S. (2006) Salicylic Acid Technical: Acute Inhalation Toxicity Study in Rats: Amended Final Report. Project Number: 9582/05. Unpublished study prepared by Stillmeadow, Inc. 24 p.	14-Aug- 2007
47206711	Jia, S. (2006) Salicylic Acid Technical: Acute Dermal Toxicity Study in Rabbits: Amended Final Report. Project Number: 9581/05. Unpublished study prepared by Stillmeadow, Inc. 18 p.	14-Aug- 2007
47206712	Kaminsky, M. (2006) Salicylic Acid Technical: Accelerated Storage Stability: Final Report. Project Number: 9578/05. Unpublished study prepared by Stillmeadow, Inc. 12 p.	14-Aug- 2007
47206713	Aiguo, Z.; Wang, D. (2005) Product Identity and Composition, Description of the Materials Used, Description of the Production Process and Discussion of the Formation of Impurities for Salicylic Acid (SA) Technical. Project Number: LTB/02018. Unpublished study prepared by LT Biosyn, Inc. 20 p.	14-Aug- 2007
47206714	Shi, X.; Xu, F. (2005) Preliminary Analysis, Certified Limits and Enforcement Analytical Method for Salicylic Acid Technical. Project Number: NCA/02018. Unpublished study by LT Biosyn, Inc. 34 p.	14-Aug- 2007
47229500	NCA Biotech, Inc. (2007) Submission of Toxicity Data in Support of the Application for Registration of Technical Salicylic Acid. Transmittal of 1 Study.	13-Sep- 2007
47229501	Gallagher, S.; Martin, K.; Beavers, J. (2006) Salicylic Acid Technical: A Dietary LC50 Study with the Northern Bobwhite. Project Number: 627/101. Unpublished study prepared by Wildlife International, Ltd. 56 p.	13-Sep- 2007
47464500	U.S. Environmental Protection Agency (2008) Submission of Risk, Exposure, Toxicity and Safety Data. Transmittal of 50 Studies.	02-Jul- 2008
47464504	Ridout, G.; Guy, R. (1988) Structure-Penetration Relationships in Percutaneous Absorption. Pesticide Formulations: Innovations and Developments: 112-123.	02-Jul- 2008
47760900	NCA Biotech, Inc. (2009) Submission of Fate, Toxicity and Product Chemistry Data in Support of the Application for Registration of Technical Salicylic Acid. Transmittal of 46 Studies.	22-May- 2009
47760901	Millar, R.; Kay, J. (2009) Background Information of Salicylic Acid. Project Number: NCA/200901. Unpublished study prepared by NCA Biotech, Inc. 7 p.	22-May- 2009

MRID No.	Citation	Receipt Date
47760902	Raskin, I. (1992) Salicylic, A New Plant Hormone. Plant Physiology 99: 799-803.	22-May- 2009
47760903	Metraux, J. (2002) Recent Breakthroughs in the Study of Salicylic Acid Biosynthesis. Trends in Plant Science 7(8): 332-334.	22-May- 2009
47760904	Silverman, P; Seskar, M.; Kanter, D.; et al. (1995) Salicylic Acid in Rice. Plant Physiology 108: 633-639.	22-May- 2009
47760905	Coquoz, J.; Buchala, A.; Metraux, J. (1998) The Biosynthesis of Salicylic Acid in Potato Plants. Plant Physiology 117: 1095-1101.	22-May- 2009
47760906	Chen, Z.; Klessig, D. (1991) Identification of a Soluble Salicylic Acid-Binding Protein that may Function in Signal Transduction in the Plant Disease-Resistance Response . National Academy of Science, USA 88: 8179-8183.	22-May- 2009
47760907	Delaney, T.; Friedrich, L.; Ryals, J. (1995) Arabidopsis Signal Transduction Mutant Defective in Chemically and Biologically Induced Disease Resistance. Proceedings, National Academy of Science USA 92(JUL): 6602-6606.	22-May- 2009
47760909	Gaffney, T.; Friedrich, L.; Vernooij, B.; et al. (1993) Requirement of Salicylic Acid for the Induction of Systemic Acquired Resistance. Science 261: 754-755.	22-May- 2009
47760910	Hunt, M.; Neuenschwander, R.; Delaney, T.; et al. (1996) Recent Advances in Systemic Acquired Resistance Research - A Review. Gene 179: 89-95.	22-May- 2009
47760911	Jirage, D.; Tootle, T.; Reuber, T.; et al. (1999) Arabidopsis Thaliana PAD4 Encodes a Lipase-Like Gene that is Important for Salicylic Acid Signaling. National Academy of Sciences 96(23): 13583-13588.	22-May- 2009
47760912	Kumar, D.; Klessig, D. (2003) High-Affinity Salicylic Acid-Binding Protein 2 is Required for Plant Innate Immunity and Has Salicylic Acid-Stimulated Lipase Activity. National Academy of Science 100(26): 16101-16106.	22-May- 2009
47760913	Metraux, J.; Signer, H.; Ryals, J.; et al. (1990) Increase in Salicylic Acid at the Onset of Systemic Aquired Resistance in Cucumber. Science 250: 1004-1006.	22-May- 2009
47760914	Nawrath, C.; Metraux, J. (1999) Salicylic Acid Induction-Deficient Mutants of Arabidopsis Express PR-2 amd PR-5 and Accumulate High Levels of Camalexin after Pathogen Inoculation. The Plant Cell 11: 1393-1404.	22-May- 2009
47760915	Rairdan, G.; Delaney, T. (2002) Role of Salicylic Acid and N1M1/NPR1 in Race-Specific Resistance in Arabidopsis. Genetics 161: 803-811.	22-May- 2009
47760916	Rasmussen, J.; Hammerschmidt, R.; Zook, M. (1991) Systemic Induction of Salicylic Acid Accumulation in Cucumber after Inoculation with Pesudomonas Syringae PV Syringae. Plant Physiology 97: 1342-1347.	22-May- 2009
47760917	Ryals, J.; Neuenschwander, U.; Willits, M.; et al. (1996) Systemic Acquired Resistance. The Plant Cell 8: 1809-1819.	22-May- 2009
47760918	Shah, J. (2003) The Salicylic Acid Loop in Plant Defense. Current Opinion in Plant Biology 6: 365-371.	22-May- 2009

MRID No.	Citation	Receipt Date
47760919	Shulaev, V.; Leon, J.; Raskin, I. (1995) Is Salicylic Acid a Translocated Signal of Systemic Acquired Resistance in Tobacco? The Plant Cell 7: 1691-1701.	22-May- 2009
47760920	Yalpani, N.; Silverman, P.; Wilson, T.; et al. (1991) Salicylic Acid is a Systemic Signal and an Inducer of Pathogenesis-Related Proteins in Virus-Infected Tobacco. The Plant Cell 3: 809-818.	22-May- 2009
47760921	Zhang, Y.; Tessaro, M.; Lassner, M.; et al. (2003) Knockout Analysis of Arabidopsis Transcription Factors TGA2, TGA5 and TGA6 Reveals Their Redundant and Essential Roles in Systemic Acquired Resistance. The Plant Cell 15: 2647-2653.	22-May- 2009
47760922	Zhang, Y.; Fan, W.; Kinkema, M.; et al. (1999) Interaction of NPR1 with Basic Leucine Zipper Protein Transcription Factors that Bind Sequences Required for Salicylic Acid Induction of PR-1 Gene. Proceedings of the National Academy od Sciences 96: 6523-6528.	22-May- 2009
47760923	Wildermuth, M.; Dewdnwy, J.; Wu, G.; et al. (2001) Isochorismate Synthase is Required to Synthesize Salicylic Acid for Plant Defense. Nature 414: 562-571.	22-May- 2009
47760924	Gutierrez-Coronado, M.; Trejo-Lopez, C.; Larque-Saavedra, A. (1998) Effects of Salicylic Acid on the Growth of Roots and Shoots in Soybean. Plant Physiology and Biochemistry 36(8): 563-565.	22-May- 2009
47760925	Abreu, M.; Munne-Bosch, S. (2008) Salicylic acid may be Involved in the Regulation of Drought-Induced Leaf Senescence in Perennials: A Case Study in Field Grown Salvia Oficinalis L. Plants. Environmental and experimental Botany 64: 105-112.	22-May- 2009
47760926	Srivastava, M.; Dwivedi, U. (1999) Delayed Ripening of Banana Fruit by Salicylic Acid. Plant Science 158: 87-96.	22-May- 2009
47760927	Babalar, M.; Asghari, M.; Talaei, A.; et al. (2006) Effect of Pre- and Postharvest Salicylic Acid Treatment on Ethylene Production, Fungal Decay and Overall Quality of Selva Strawberry Fruit. Food Chemistry 105: 449-453.	22-May- 2009
47760928	Zhang, Y.; Chen, K.; Zhang, S.; et al. (2002) The Role of Salicylica Acid in Postharvest Ripening of Kiwifruit. Postharvest Biology and Technology 28: 67-74.	22-May- 2009
47760929	Rajjou, L.; Belghazi, M.; Huguet, R.; et al. (2006) Proteomic Investigation of the Effect of Salicylic Acid on Arabidopsis Seed Germination and Establishment of Early Defense Mechanisms. Plant Physiology 141: 910-923.	22-May- 2009
47760930	Janssen, K.; Hollman, P.; Venema, D.; et al. (1996) Salicylates in Foods. Nutrition Reviews 54: 357-359.	22-May- 2009
47760931	Kay, J. (2009) Supplement to 47206713; Additional Manufacturing Process Information (Salicylic Acid). Project Number: NCA/200902. Unpublished study prepared by NCA Biotech, Inc. 33 p.	22-May- 2009
47760932	Kay, J. (2009) Summary of Salicylic Acid Toxicity Data. Project Number: NCA/200903. Unpublished study prepared by NCA Biotech, Inc. 8 p.	22-May- 2009
47760933	Fiume, M. (2003) Safety Assessment of Salicylic Acid, Butyloctyl Salicylate, Calcium Salicylate, C12-15 Alkyl Salicylate, Capryloyl Salicylic Acid, Hexyldodecyl Salicylate, Isodecyl Salicylate, Magnesium Salicylate, MEA-Salicylate, Ethylhexyl Salicylate, Potassium Salicylate, Methyl Salicylate, Myristyl Salicylate, Sodium Salicylate, TEA-Salicylate, and Tridecyl Salicylate. International Journal of Toxicology 22: 1-108.	22-May- 2009

MRID No.	Citation	Receipt Date
47760934	Scientific Committee on Cosmetic Products and Non-Food Products (2002) Opinion of the Scientific Committee on Cosmetic Products and Non-Food Products Intended for Consumers Concerning Salicylic Acid. 36p.	22-May- 2009
47760935	Rocher, F.; Chollet, J.; Jousse, C.; et al. (2006) Salicylic Acid, an Ambimobile Molecule Exhibiting a High Ability to Accumulate in the Phloem. Plant Physiology 141: 1684-1693.	22-May- 2009
47760936	Metwally, A.; Finkemeier, I.; Georgi, M.; et al. (2003) Salicylic Acid Alleviates the Cadmium Toxicity in Barley Seedlings. Plant Physiology 132: 272-281.	22-May- 2009
47760937	Scotter, M.; Roberts, D.; Wilson, L.; et al. (2006) Free Salicylic Acid and Acetyl Salicylic Acid Content of Foods Using Gas Chromatography-Mass Spectrometry. Food Chemistry 105: 273-279.	22-May- 2009
47760938	Amann, R.; Peskar, B. (2002) Anti-Inflammatory Effects of Aspirin and Sodium Salicylate. European Journal of Pharmacology 447: 1-9.	22-May- 2009
47760939	Shakirova, F. (2007) Role of Hormonal System in the Manifestation of Growth Promoting and Antistress Action of Salicylic Acid. Biochemistry. The Netherlands: Springer.	22-May- 2009
47760941	Foltinova, P.; Grones, J. (1996) Euglena gracilis as an Eukaryotic Test Organism for Detecting Mutagens and Antimutagens (Salicylic Acid). Mutation Research 393: 1-6.	22-May- 2009
47760942	San, R.; Chan, R. (1986) Inhibitory Effect of Phenolic Compounds on Aflatoxin B1 Metabolism and Induced Mutagenesis (Salicylic Acid). Mutation Research 177: 229-239.	22-May- 2009
47760943	Sheu, C.; Salomon, D.; Simmons, J.; et al. (1974) Inhibitory Effects of Lipophilic Acids and Related Compounds on Bacteria and Mammalian Cells. Antimicrobial Agents and Chemotherapy 7: 349-363.	22-May- 2009
47760944	Kleinerman, E.; Louie, J.; Wahl, L.; et al. (1980) Pharmacology of Human Spontaneous Monocyte-Mediated Cytotoxicity. Arthritis and Rheumatism 24: 774-780.	22-May- 2009
47760946	Waltman, R.; Tricomi, V.; Shabanah, E.; et al. (1973) The Effect of Anti-Inflammatory Drugs on Parturition Parameters in the Rat. Prostaglandins 4: 93-106.	22-May- 2009
47760947	Tanaka, S.; Kawashima, K.; Nakaura, S.; et al. (1973) Studies on Teratogenic Effects of Salicylic Acid and Aspirin in Rats as Related to Fetal Distribution. Cong. Anom. 13: 73-84.	22-May- 2009
47760948	Jones, A. (1994) Surprising Signals in Plant Cells. Science 263(Jan 14): 183-184.	22-May- 2009
47760949	Morris, K.; Mackerness, S.; Page, T.; et al. (2000) Salicylic Acid Has a Role in Regulating Gene Expression During Leaf Senescence. The Plant Journal 23: 677-685.	22-May- 2009
47775300	NCA Biotech, Inc. (2009) Submission of Toxicity Data in Support of the Registration of Technical Salicylic Acid. Transmittal of 3 Studies.	11-Jun- 2009
47775301	Delaney, T.; Uknes, S.; Vernooij, B.; et al. (1994) A Central Role of Salicylic Acid in Plant Disease Resistants. Science 266: 1247-1249.	11-Jun- 2009
47775302	McCann, J.; Choi, E.; Yamasaki, E.; et al. (1995) Detection of Carcinogens as Mutagens in the Salmonella/ Microsome Test: Assay of 300 Chemicals. Proceedings of National Academy of Science 72(12): 5135-5139.	11-Jun- 2009

MRID No.	Citation	Receipt Date
47775303	Commoner, B. (1976) Reliability of Bacterial Mutagenesis Techniques to Distinguish Carcinogenic and Noncarcinogenic Chemicals. Project Number: EPA/600/1/76/022, 68/01/2471. Unpublished study prepared by Washington University. 113 p.	11-Jun- 2009
48224600	Loveland Products, Inc. (2010) Submission of Product Chemistry, Toxicity and Fate Data in Support of the Application for Registration of LPI 6194 Concentrate. Transmittal of 5 Studies.	14-Sep- 2010
48224601	Wo, C. (2010) LPI 6194 Concentrate: Physical and Chemical Characteristics: Color, Physical State, Odor, Flammability, pH, Viscosity, and Density/Relative Density. Project Number: 29844, P801. Unpublished study prepared by Eurofins/Product Safety Laboratories. 16 p.	14-Sep- 2010
48224602	Knox III, D. (2010) LPI 6194 Concentrate: Enforcement Analytical Method for the Determination of Salicylic Acid by High Pressure Liquid Chromatography. Project Number: 29843. Unpublished study prepared by Eurofins/Product Safety Laboratories. 10 p.	14-Sep- 2010
48224603	Tillman, A. (2010) LPI 6194 Concentrate: Waiver Requests for Certain Phys-Chem Property Data. Project Number: LPI/2010017. Unpublished study prepared by Loveland Products, Inc. 6 p.	14-Sep- 2010
48224604	Tillman, A. (2010) LPI 6194 Concentrate and LPI 6194 RTU: Waiver Request for Tier I Mammalian Toxicity Data. Project Number: LPI/201021. Unpublished study by Loveland Products, Inc. 10 p.	14-Sep- 2010
48224605	Tillman, A. (2010) LPI 6194 Concentrate and LPI 6194 RTU: Summary of Tier I Nontarget Organism Data Requirements. Project Number: LPI/201020. Unpublished study by Loveland Products, Inc. 27 p.	14-Sep- 2010
48224700	Loveland Products, Inc. (2010) Submission of Product Chemistry and Toxicity Data in Support of the Application for Registration of LPI 6194 RTU. Transmittal of 3 Studies.	14-Sep- 2010
48224701	Tillman, A. (2010) Product Identity and Composition, Description of the Materials Used, Description of the Formulation Process, Discussion of the Formation of Impurities, Certified Limits, and Enforcement Analytical Method for LPI 6194 RTU. Project Number: LPI/201022. Unpublished study prepared by Loveland Products, Inc. 84 p.	14-Sep- 2010
48224702	Tillman, A. (2010) LPI 6194 RTU: Phys-Chem Characteristics Data and Waiver Requests for Certain Data. Project Number: LPI/2010015. Unpublished study by Loveland Products, Inc. 12 p.	14-Sep- 2010
48224703	Tillman, A. (2010) LPI 6194 RTU: Request to Bridge Acute Toxicity Data. Project Number: LPI/201016. Unpublished study prepared by Loveland Products, Inc. 21 p.	14-Sep- 2010
48225200	Loveland Products, Inc. (2010) Submission of Product Chemistry, Toxicity and Fate Data in Support of the Application for Registration of Salicylic Acid Technical. Transmittal of 13 Studies.	14-Sep- 2010
48225201	Sinning, D. (2010) Physical and Chemical Characteristics of 98.7% Salicylic Acid Technical: Stability, Oxidation/Reduction, pH, UV/Vis, Partition Coefficient (n-Octanol/Water) and Water Solubility: Final Report. Project Number: 4670/01. Unpublished study by Case Consulting Laboratories, Inc. 29 p.	14-Sep- 2010
48225202	Tillman, A. (2010) Summary of and Waiver Request for Physical and Chemical Properties of Salicylic Acid Technical. Project Number: LPI/201018. Unpublished study by Loveland Products, Inc. 11 p.	14-Sep- 2010
48225203	Hauswirth, J. (2010) Summary of the Acute Toxicity of Salicylic Acid. Project Number: LPI/201008. Unpublished study prepared by Loveland Products, Inc. 13 p.	14-Sep- 2010
48225204	Hauswirth, J. (2010) Subchronic Toxicity of Salicylic Acid. Project Number: LPI/201009. Unpublished study prepared by Loveland Products, Inc. 99 p.	14-Sep- 2010

MRID No.	Citation	Receipt Date
48225205	Hauswirth, J. (2010) Developmental and Reproduction Toxicity of Salicylic Acid. Project Number: LPI/201012. Unpublished study prepared by Loveland Products, Inc. 175 p.	14-Sep- 2010
48225206	Hauswirth, J. (2010) Metabolism of Salicylic Acid. Project Number: LPI/201011. Unpublished study prepared by Loveland Products, Inc. 50 p.	14-Sep- 2010
48225207	Hauswirth, J. (2010) Mutagenicity and Genotoxicity for Salicylic Acid. Project Number: LPI/201010. Unpublished study prepared by Loveland Products, Inc. 137 p.	14-Sep- 2010
48225208	Hauswirth, J. (2010) Dermal Penetration of Salicylic Acid. Project Number: LPI/201013. Unpublished study prepared by Loveland Products, Inc. 45 p.	14-Sep- 2010
48225209	Tillman, A. (2010) Summary of Tier 1 Nontarget Organism Data Requirements for Salicylic Acid Technical. Project Number: LPI/201019. Unpublished study by Loveland Products, Inc. 24 p.	14-Sep- 2010
48225210	Porch, J.; Krueger, H. (2010) LPI 6194 Concentrate: A Toxicity Test to Determine the Effects of the Test Substance on Seedling Emergence of Ten Species of Plants: Final Report. Project Number: 224/102. Unpublished study prepared by Wildlife International, Ltd. 68 p.	14-Sep- 2010
48225211	Porch, J.; Krueger, H. (2010) LPI 6194: A Toxicity Test to Determine the Effects of the Test Substance on Vegetative Vigor of Ten Species of Plants: Final Report. Project Number: 224/103. Unpublished study prepared by Wildlife International, Ltd. 87 p.	14-Sep- 2010
48225212	Porch, J.; Krueger, H. (2010) Salicylic Acid Technical: An Acute Contact Toxicity Study with the Honey Bee: Final Report. Project Number: 224/101. Unpublished study prepared by Wildlife International, Ltd. 21 p.	14-Sep- 2010
48225213	Tillman, A. (2010) Salicylic Acid Mode of Action. Project Number: LPI/201014. Unpublished study prepared by Loveland Products, Inc. 153 p.	14-Sep- 2010
48562300	Loveland Products, Inc. (2011) Submission of Product Chemistry Data in Support of the Application for Registration of LPI 6194 RTU. Transmittal of 2 Studies.	
48562301	Tillman, A. (2011) Product Identity and Composition, Description of Starting Materials, Production and Formulation Process for LPI 6194 RTU: Supplemental Report to MRID 48224701. Project Number: LPI/201108. Unpublished study prepared by Loveland Products, Inc. 26p.	
48562302	Wo, C. (2011) LPI 6307: Physical and Chemical Characteristics: pH. Project Number: 32722 P8001. Unpublished study prepared by Eurofins/Product Safety Laboratories. 11p.	
48562400	Loveland Products, Inc. (2011) Submission of Product Chemistry and Toxicity Data in Support of the Application for Registration of LPI 6134 Concentrate. Transmittal of 7 Studies.	
48562401	Tillman, A. (2011) Product Identity and Composition, Description of Starting Materials, Production and Formulation Process for LPI 6194 Concentrate: Supplemental Report to MRID 46964301. Project Number: LPI/201107. Unpublished study prepared by Loveland Products, Inc. 76p.	
48562402	Durando, J. (2010) LPI 6194 Concentrate: Acute Oral Toxicity Up and Down Procedure in Rats. Project Number: 39845 P320/UDP. Unpublished study by Eurofins/Product Safety Laboratories. 16p.	
48562403	Durando, J. (2010) LPI 6194 Concentrate: Acute Dermal Toxicity Study in Rats - Limit Test. Project Number: 29846 P322/RAT. Unpublished study prepared by Eurofins/Product Safety Laboratories. 15p.	

MRID No.	Citation		
48562404	Durando, J. (2010) LPI 6194 Concentrate: Acute Inhalation Toxicity Study in Rats. Project Number: 29847 P330. Unpublished study prepared by Eurofins/Product Safety Laboratories. 23p.		
48562405	Durando, J. (2010) LPI 6194 Concentrate: Primary Eye Irritation Study in Rabbits. Project Number: 29848 P324. Unpublished study prepared by Eurofins/Product Safety Laboratories. 16p.		
48562406	Durando, J. (2010) LPI 6194 Concentrate: Primary Skin Irritation Study in Rabbits. Project Number: 28949 P326. Unpublished study prepared by Eurofins/Product Safety Laboratories. 16p.		
48562407	Durando, J. (2010) LPI 6194 Concentrate:Dermal Sensitization Study-Guinea Pigs (Buehler Method). Project Number: 29850 P328. Unpublished study by Eurofins/Product Safety Laboratories. 25p.		

#### B. EPA Risk Assessment Memoranda

U.S. EPA. 2011a. Gonzales, Angela L. Science Review in Support of Salicylic Acid Technical, Containing 98.7% Salicylic Acid as Its Active Ingredient. Memorandum dated 12/8/2011.

U.S. EPA. 2011b. Gonzales, Angela L. Science Review in Support of Salicylic Acid Technical, Containing 98.7% Salicylic Acid as Its Active Ingredient. Memorandum dated 06/16/2011.

#### C. References

Hazardous Substances Data Bank (HSDB). 2008. "Salicylic Acid". U.S. Department of Health and Human Services, National Library of Medicine. March 31, 2011.

< http://www.toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~TE3afi:1>

U.S. EPA 2008. Terrestrial Residue Exposure Model (T-REX) Version 1.4.1. EFED/OPP/USEPA.



#### October 14, 2008

#### Web Site Addresses on Pesticide Product Labeling

The Office of Pesticide Programs (OPP) has received multiple questions about placing website addresses on pesticide products and is developing a more in-depth response to discuss how the OPP expects to evaluate website content. For the time being, references to websites may be placed on labels. Be aware that adding such a reference transforms the website into labeling under FIFRA sec. 2(p)(2) and the website is subject to review by the Agency. If the website content is false or misleading, the product would be misbranded and its sale or distribution unlawful under FIFRA sec. 12(a)(1)(E). In addition, regardless of whether a website is referenced on a product's label, claims made on the website may not substantially differ from those claims approved through the registration process. Although EPA has not yet determined the extent to which it will routinely review company websites, if the Agency finds or if it is brought to our attention that a website contains false or misleading statements or claims substantially differing from claims approved through the registration process, the website may be referred to EPA's Office of Enforcement and Compliance Assurance.



# **US Environmental Protection Agency Office of Pesticide Programs**

BIOPESTICIDES REGISTRATION ACTION DOCUMENT

Potassium Silicate PC Code 072606

September 7, 2007

# **BIOPESTICIDES REGISTRATION ACTION DOCUMENT**

# **Potassium Silicate**

PC Code 072606 September 7, 2007

U.S. Environmental Protection Agency Office of Pesticide Programs Biopesticides and Pollution Prevention Division Potassium Silicate (PC Code 072606)

#### **Table of Contents**

#### I. Executive Summary

#### II. Overview

- A. ACTIVE INGREDIENT OVERVIEW
- B. USE PROFILE
- C. ESTIMATED USAGE
- D. DATA REQUIREMENTS
- E. REGULATORY HISTORY
- F. CLASSIFICATION
- G. FOOD CLEARANCES/TOLERANCES

#### **III. Science Assessment**

#### A. PHYSICAL/CHEMICAL PROPERTIES ASSESSMENT

- 1. Product Identity and Mode of Action
  - a. Product Identity
  - b. Mode of Action
- 2. Physical and Chemical Properties Assessment

#### B. HUMAN HEALTH ASSESSMENT

- 1. Toxicology Assessment
  - a. Acute Toxicity
  - b. Genotoxicity, Immune Response, Mutagenicity, Developmental, Oncogenicity, Subchronic and Chronic Toxicity
  - c. Effects on the Endocrine System
- 2. Dose Response Assessment
- 3. Aggregate Exposure and Risk Characterization
  - a. Dietary
    - i. Food
    - ii. Drinking Water
  - b. Other Non-occupational Exposure
- 4. Occupational, Residential, School and Day care Exposure and Risk Characterization
  - a. Occupational Exposure and Risk Characterization
  - b. Residential, School and Day Care Exposure and Risk Characterization
- 5. Acute and Chronic Dietary Risks for Sensitive Subpopulations Particularly Infants and Children
- 6. Aggregate Exposure from Multiple Routes Including Dermal, Oral, and Inhalation
- 7. Cumulative Effects
- 8. Risk Characterization

#### C. ENVIRONMENTAL ASSESSMENT

- 1. Ecological Effects Hazard Assessment: Tier I Non-Target Organisms
  - a. Avian Acute Toxicity and Avian Dietary Toxicity
  - b. Freshwater Fish Acute Toxicity

- c. Aquatic Invertebrate Acute Toxicity
- d. Non-Target Plant Toxicity
- e. Non-Target Insect Toxicity
- 2. Environmental Fate and Ground Water Data
- 3. Ecological Exposure and Risk Characterization
  - a. Environmental Exposure Assessment
  - b. Naturally-Occurring Potassium and Siliconi. Potassium
    - ii. Silicon
- D. EFFICACY DATA

#### IV. Risk Management Decision

- A. DETERMINATION OF ELIGIBILITY FOR REGISTRATION
- **B. REGULATORY POSITION** 
  - 1. Unconditional Registration
  - 2. Exemption from the Requirement of a Tolerance for Food Uses
  - 3. CODEX Harmonization
  - 4. Nonfood Registrations
  - 5. Risk Mitigation
  - 6. Endangered Species Statement
- C. LABELING RATIONALE
  - 1. Human Health Hazard
    - a. Worker Protection Standard
    - b. Non-Worker Protection Standard
    - c. Precautionary Labeling
  - 2. Environmental Hazards Labeling
  - 3. Application Rate
- D. LABELING
- V. Actions Required by Registrants
- VI. Appendix A
- VII. References

#### BIOPESTICIDES REGISTRATION ACTION DOCUMENT TEAM

## **Office of Pesticide Programs:**

# **Biopesticides and Pollution Prevention Division**

# **Biochemical Pesticides Branch**

Sheryl K. Reilly, Ph.D. Biologist, Branch Chief Linda A. Hollis Microbiologist, Team Leader

Manying Xue Chemist, Health Effects/Product Chemistry Russell S. Jones, Ph.D. Biologist, Health Effects/Nontarget Organisms

Carol E. Frazer, Ph.D. Toxicologist, Regulatory Action Leader

#### I. Executive Summary

Potassium silicate is the potassium salt of silicic acid, and, in formulation, is readily absorbed by the plant. Silicon comprises 32% of the Earth's crust, and silicic acid salts (silicates) are the most common form of silicon. Consequently exposure to silicates is widespread in activities involving contact with soil and natural water. The other part of the chemical, potassium is a required element for survival of both plants and animals, as is silicon.

Potassium silicate is an active ingredient to be used as a fungicide, insecticide and miticide. Potassium silicate will be used as a broad spectrum, preventative fungicide with optimum control obtained when used under a scheduled preventative spray program. Potassium silicate also provides suppression of mites, whiteflies, and other insects. It is approved for use on agricultural crops, fruits, nuts, vines, turf and ornamentals.

Data and information addressing the mammalian and non-target toxicology data requirements were submitted and adequately satisfy data requirements to support the registration. No additional data are needed to support registration.

#### II. Overview

#### A. ACTIVE INGREDIENT OVERVIEW

**Common Name:** Potassium silicate

**Chemical Name:** Potassium salt of silicic acid

**CAS Number:** 1312-76-1

**Chemical Formula**: K<sub>2</sub>O·3.9SiO<sub>2</sub>

Molecular Weight: 328

**Trade Name**: AgSil®25, Kasil 1

**OPP Chemical Code:** 072606

**Manufacturer:** PQ Corporation

P.O. Box 840

Valley Forge, PA, 19482-0840

#### **B. USE PROFILE**

Proposed uses and application methods for potassium silicate include the following:

**Type of Pesticide:** Fungicide, miticide, insecticide

**Use Sites:** Agricultural crops, fruits, nuts, vines, turf and ornamentals

Formulation Types: Liquid

**Method and Rates of Application:** Conventional spray application equipment should be used in the field.

**Use Practice Limitations:** Do not allow workers into treated areas for four hours following application. Do not spray when and where bees are foraging.

**Timing:** Begin applications when environmental conditions are conducive to disease development. Repeat applications no sooner than every 7 days. For mite and insect suppression, begin applications when pests first appear and repeat

applications as necessary to maintain suppression, but no sooner than every 7 days. Apply up to the day of harvest (0 day PHI).

#### C. ESTIMATED USAGE

This is a new product and projected usage is not available.

#### D. DATA REQUIREMENTS

The Biopesticides and Pollution Prevention Division (BPPD) reviewed data requirements for granting this registration under Section 3(c)(5) of FIFRA. Mammalian toxicology and ecological effects data requirements for PS were fulfilled. Product analysis data requirements were adequately satisfied.

#### E. REGULATORY HISTORY

On July 27, 2005, EPA published a notice of filing acknowledging receipt of an application to register a pesticide product containing an active ingredient not currently in any other pesticidal product, and a petition (5F6905) from PQ Corporation proposing, pursuant to section 408(d) of the Federal Food, Drug, and Cosmetic Act (FFDCA), 21 U.S.C. 346a(d), to amend 40 CFR part 180 to establish an exemption from the requirement of a tolerance for the biochemical pesticide potassium salt of silicic acid (potassium silicate). The exemption from the requirement for a tolerance was published June 14, 2006 (71 FR 34267), with the caveat that it not be applied at rates exceeding 1% by weight in aqueous solution. Potassium silicate is used as a non-food use inert, but does not a tolerance exemption as an inert ingredient.

#### F. CLASSIFICATION

Potassium silicate has not been formally classified by the Biochemical Classification Committee.

#### G. FOOD CLEARANCES/TOLERANCES

FDA has determined that sodium silicate and potassium silicate can be used interchangeably. Sodium silicate has been determined to be GRAS (Generally-Recognized as Safe) by FDA (21 CFR 182.90 and 21 CFR 182.1711) for limited use in canned potable water as a corrosion inhibiting agent. Potassium silicate is also used as a corrosion inhibitor for potable water, with the use rate for municipal water supplies at 8 parts per million. Sodium silicate has been is exemption from requirement of a tolerance when used as an inert ingredient in pre and post-harvest pesticide products (40 CFR 180.910). Sodium silicate can be used as an inert as a surfactant, emulsifier, wetting agent, stabilizer, inhibitor, while there is not a food use inert

tolerance exemption for potassium silicate. Silica is also approved by the FDA for use as an anti-caking agent in food.

#### **III. Science Assessment**

#### A. PHYSICAL/CHEMICAL PROPERTIES ASSESSMENT

All product chemistry data requirements for the technical grade and the end-use products are met.

### 1. Product Identity and Mode of Action

# a. Product Identity:

The technical grade active ingredient (TGAI) consists of 99.4% potassium silicate and at this time there is one end-use product that is 29.1% potassium silicate

#### b. Mode of Action:

Potassium silicate is a dessicant.

#### 2. Physical and Chemical Properties Assessment

The physical and chemical characteristics of the TGAI were submitted to support the registration. They are summarized in Table 1.

Table 1. Product chemistry data requirements:

TABLE 1. Physical and Chemical Properties for Technical Potassium Silicate <sup>a</sup>					
Guideline Reference No./Property	Description of Result	Methods			
830.6302 Color	White				
830.6303 Physical State	Solid @ room temperature				
830.6304 Odor	Odorless				
830.6313 Stability	Stable	Not provided, not required if provided for EP			
830.6314 Oxidation/Reduction: Chemical Incompatibility	Based on known chemistry and prior practical experience, will oxidize metals	Not provided			

830.6315	Flammability	N/A <sup>1</sup>	
830.6316	Explodability	N/A	
830.6317 830.6320	Storage Stability Corrosion Characteristics	Based on typical results from container corrosion testing of other solid products, no significant reaction is expected between the TGAI/MP and the commercial packaging	
830.6319	Miscibility	N/A, product is a solid	
830.6321	Dielectric Breakdown Voltage	N/A, product not for use on electrical equipment	
830.7000	pH	N/A, product is a solid	
830.7050	UV/Visible	N/A	
830.7100	Viscosity	N/A, product is a solid	
830.7200	Melting Range	1400EF (760EC)	Not provided
830.7220	Boiling Range	N/A, product is a solid	
830.7300	Bulk Density	1.24 g/cc	Not provided
830.7370	Dissociation Constant in Water	Product is completely ionized to potassium and silicate	
830.7550	Partition Coefficient	N/A, product is a polar chemical.	
830.7840	Water Solubility	<0.336 g/L @ 25EC, increasing to 300 g/L @ 80EC. Once dissolved, material will not precipitate out	Not provided
830.7950	Vapor Pressure	N/A	

<sup>&</sup>lt;sup>a</sup> Data from MRID 46434702

#### **B. HUMAN HEALTH ASSESSMENT**

Information submitted to support the registration application of the technical grade active ingredient and the end-use product adequately satisfies the food and non-food use requirements set forth in 40 CFR 158.690 (c) for biochemical pesticides. The overall toxicological risk from human exposure to potassium silicate is negligible.

## 1. Toxicology Assessment

<sup>&</sup>lt;sup>1</sup> Not Applicable

Adequate mammalian toxicology data are available and support registration of the products containing the active ingredient potassium silicate.

# a. Acute Toxicity

TABLE 3a Acute Toxicity Profile - Technical Grade					
Guideline No.	Study Type	MRID(s)	Results	Toxicity Category	
870.1100	Acute oral [rat]	46434903	$LD_{50} = 2000 \text{ mg/kg } (80-85\% \text{ potassium silicate powder})$	III	
870.1200	Acute dermal [rat]	46434902	Moderate to low toxicity (Silica gel)	IV	
870.1300	Acute inhalation [rat]	46434906	No animal mortality (40% Silica gel), No lung damage (Silicon dioxide or silicates)	IV	
870.2400	Acute eye irritation [rabbit]	46434905	An ocular irritant (Aqueous concentrated potassium silicate) Corrosive ( > 80% concentration potassium silicate) Irritating (Sodium silicate powder)	III I	
870.2500	Acute dermal irritation [rabbit]	46434901	A dermal irritant (Aqueous concentrated potassium silicate), Corrosive( > 80% concentration potassium silicate), Not irritating (Sodium silicate powder)	III I IV	
870.2600	Skin sensitization [guinea pig]	46434904	Not a sensitizer (Laundry product containing 6% sodium silicate and 30% sodium metasilicate)	IV	

TABLE 3b Acute Toxicity Profile - End-Use Product					
Guideline No.	Study Type	MRID(s)	Results	Toxicity Category	
870.1100	Acute oral [rat]	46434903	LD <sub>50</sub> > 5,000 mg/kg (29% aqueous potassium silicate end use fungicide/insecticide)	IV	
870.1200	Acute dermal [rat]	46434902	LD <sub>50</sub> > 5,000 mg/kg (AgSil®25, a 29% potassium silicate aqueous solution)	IV	

870.1300	Acute inhalation [rat]	46434906	> 2.06 mg/L (AgSil®25, a 29% potassium silicate aqueous solution)	IV
870.2400	Acute eye irritation [rabbit]	46434905	Irritation cleared within 7 days (Kasil 1, unknown percentage of potassium silicate aqueous solution),	III
870.2500	Acute dermal irritation [rabbit]	46434901	Slightly irritating; irritation cleared within 72 hours (Kasil 1, unknown percentage of potassium silicate in aqueous solution)	IV
870.2600	Skin sensitization [guinea pig]	46434904	Not sensitizing (AgSil®25)	IV

# b. Genotoxicity, Immune Response, Mutagenicity, Developmental, Oncogenicity, Subchronic and Chronic Toxicity

Waiver requests (MRID 464347-01) were submitted for 90-day oral toxicity (OPPTS 870.3100), genotoxicity (OPPTS 870.5100; 870.5300; 870.5375), teratogenicity (OPPTS 870.3700) and immunotoxicity (OPPTS 880.3550) for the active ingredient potassium silicate.

The registrant also submitted an evaluation article prepared by the Joint FAO/WHO (Food and Agriculture Organization of the United Nations/World Health Organization) Expert Committee on Food Additives which met in Geneva, 25 June - 4 July 1973, World Health Organization, Geneva 1974.

In the article, the previously published monograph has been expanded and reproduced. The available data from the seventeenth report regarding silicon dioxide and certain silicates for biochemical aspects and toxicological aspects including special studies on carcinogenicity and special studies on reproduction have been summarized and discussed.

The Joint FAO/WHO Expert Committee concluded available data on orally administered silica and silicates, including flumed silicon dioxide, appear to substantiate the biological inertness of these compounds. Any silicate absorbed is excreted by the kidneys without evidence of toxic accumulation in the body, except for the reported damage to dog kidney by magnesium trisilicate and sodium silicate. Methods for estimating silica in body tissues have been greatly improved in recent years making some of the earlier data somewhat less valuable. A number of short-term studies in two species are available. Talc and magnesium silicate are specified free from asbestos-like particles. This stipulation is made while acknowledging the fact that existing methods for estimating asbestos-like particles in talc and magnesium silicate are not yet fully adequate. Excluding the silicates magnesium silicate and talc, FAO/WHO's estimate of acceptable daily intake for man for silicon dioxide and certain silicates is "Not limited."

FDA has determined that sodium silicate and potassium silicate can be used interchangeably. Sodium silicate has been determined to be GRAS (Generally-Recognized as Safe) by FDA (21 CFR 182.90 and 21 CFR 182.1711) for limited use in canned potable water as a corrosion inhibiting agent.

Sodium silicate has been registered with an exemption from the requirement for a tolerance (40 CFR 180.910) as surfactant, emulsifier, wetting agent, stabilizer, or inhibitor. Solutions of potassium silicate are used in potable water for corrosion protection. Potassium silicates are sold as fertilizer

Comprehensive reviews of soluble silicates, including potassium silicates (HERA, 2005), potassium silicate fertilizers (NOSB/TAP, 2003), and the Silicon Dioxide and Silica Gel RED (EPA, 1991) indicate there will be no human health concerns when the end-use product is used in accordance with accepted labeling.

Therefore, BPPD concludes the submitted information in support of the requested toxicity waivers for 90-Day Oral Toxicity (OPPTS 870.3100), Genotoxicity (OPPTS 870.5100; 870.5300; 870.5375), Teratogenicity (OPPTS 870.3700) and Immunotoxicity (OPPTS 880.3550) is acceptable.

#### c. Effects on the Endocrine System

BPPD has considered, among other relevant factors, available information concerning whether potassium silicate may have an effect in humans similar to an effect produced by a naturally occurring estrogen or other endocrine effects. There is no known related chemical that acts as an endocrine disruptor. The Agency concludes that there will be no incremental adverse effects to the endocrine system.

#### 2. Dose Response Assessment

No toxicological endpoints are identified.

# 3. Aggregate Exposure and Risk Characterization

# a. Dietary

#### i. Food

In the absence of any toxicological endpoints, risk from the consumption of residues is not expected for the general population, including infants and children.

# ii. Drinking Water

Treatment of crops in the fields may include run-off to surface and ground water, but the compound is ubiquitous and cannot be distinguished from natural sources.

# b. Other Non-occupational Exposure

Potassium silicate is ubiquitous in the environment so there is routinely exposure to it without toxic effects.

# 4. Occupational, Residential, School and Day Care Exposure

Human exposure to potassium silicate is expected in residential, school and day care areas, as everyone is daily exposed to potassium silicate in dust, dirt, soil, etc. The additional amount of potassium silicate found in foodstuff as a result of the use of the subject pesticidal products is expected to be minuscule compared to these other sources.

# a. Occupational Exposure

Agricultural use of potassium silicate is subject to the Worker Protection Standards (WPS), requiring Personal Protective Equipment (PPE) a long-sleeved shirt, long pants, socks, shoes and gloves, plus a 4 hour Restricted Entry Interval (REI).

# b. Residential, School and Day Care Exposure and Risk Characterization

In the absence of any toxicological endpoints, risk from the consumption of residues is not expected for populations in residential, school and day care settings, including infants and children.

# 5. Acute and Chronic Dietary Risks for Sensitive Subpopulations Particularly Infants and Children

FFDCA section 408 provides that EPA shall apply an additional tenfold margin of exposure (safety) for infants and children in the case of threshold effects to account for pre- and post-natal toxicity and the completeness of the database unless EPA determines that a different margin of exposure (safety) will be safe for infants and children. Margins of exposure (safety) are often referred to as uncertainty (safety) factors. In this instance, based on all the available information, the Agency concludes that potassium silicate is practically non-toxic to mammals, including infants and children. Thus, there are no threshold effects of concern and, as a result, the provision requiring an additional margin of safety does not apply. Further, the provisions of

consumption patterns, special susceptibility, and cumulative effects do not apply. And, as no toxic endpoints have been identified, any hazard is impossible to determine. As a result, EPA has not used a margin of exposure (safety) approach to assess the safety of potassium silicate.

# 6. Aggregate Exposure from Multiple Routes Including Dermal, Oral, and Inhalation

Aggregate exposure to potassium silicate by field workers and applicators may occur via oral, dermal and inhalation routes. These risks are measured via the acute toxicity studies submitted to support registration. As the oral toxicity study for PS showed no toxicity at the maximum dose tested (2,000 mg/kg) (Toxicity Category III), the risks anticipated from oral exposure are considered to be minimal.

Because the inhalation toxicity studies for potassium silicate showed no toxicity either (Toxicity Category IV), the risks anticipated for this route of exposure are also considered minimal

Results of the acute dermal toxicity study indicated moderate to low toxicity at the maximum dose tested, although dermal irritation was observed (Toxicity Category III). Based on these results, the anticipated risks from dermal exposure are also considered to be of low consequence.

Therefore, the risks from aggregate exposure via oral, dermal and inhalation exposure are a compilation of three low risk exposure scenarios and are considered negligible.

#### 7. Cumulative Effects

Potassium silicate is not toxic and therefore cumulative effects from common mechanisms of toxicity are not possible.

#### 8. Risk Characterization

The Agency has considered potassium silicate in light of the relevant safety factors in FQPA and FIFRA. A determination has been made that no unreasonable adverse effects to the U.S. population in general, and to infants and children in particular, will result from the use of potassium silicate when label instructions are followed.

#### C. ENVIRONMENTAL ASSESSMENT

Comprehensive reviews have already been conducted on potassium silicate effects on the environment and non-target organisms by the Human Environmental Risk Assessment On Ingredients of European Household Cleaning Products (HERA, 2005), including the related

soluble silicates sodium silicate and sodium metasilicate, and by the National Organic Standards Board/Technical Advisory Panel (NOSB/TAP, 2003) for its use as a fertilizer. Both reviews concluded that the use of potassium silicate was unlikely to result in any adverse effects to the environment or non-target organisms for the aforementioned uses. Additionally, the Silicon Dioxide and Silica Gel RED (EPA/OPP, 1991) states that products containing silicon dioxide and silica gel, when used in accordance with accepted labeling, will not present hazards to non-target organisms or the environment. Potassium and silica are ubiquitous in terrestrial and aquatic environments and are essential nutrients in plants and animals (Anderson et al., 2005; Mengel and Kirby, 1978; Nielson, 1991; review by Savant et al., 1999). Potassium and silica respectively comprise approximately 2.59% and 32% of the Earth's crust by weight (Mengel and Kirby, 1978; review by Savant et al., 1999).

A detailed EPA review of the available public information and information submitted by the registrant in support of non-target organism waiver requests is presented below. In certain instances, information/data regarding sodium silicate was used when similar information/data for potassium silicate were unavailable. According to FDA (Chao, 1978) and HERA (2005), potassium silicate and sodium silicate have enough chemical similarity to be used interchangeably for purposes of risk assessment.

# 1. Ecological Effects Hazard Assessment: Tier I Non-Target Organisms

When applied according to the proposed label directions, no direct exposure of birds or aquatic organisms to the end use product is expected to occur. Many published studies were supplied to the Agency which indicates potential environmental/ecological effects from potassium silicate are likely to be negligible.

# a. Avian Acute Toxicity and Avian Dietary Toxicity

No Guideline studies (OPPTS 850.2100 & 850.2200) were submitted. In lieu of Guideline studies, the registrant submitted a non-guideline avian dietary study (see Table 1) obtained from the public literature; an additional non-Guideline study was also reviewed by EPA. In both studies, no apparent toxicity resulted from short-term, sub-chronic consumption of dietary silicon. Dietary exposure of applied potassium silicate to birds is likely to be low and will not exceed exposure to potassium and silicates that are already present in the environment, particularly in many plants and in natural waters. Naturally-occurring potassium and silica are present at levels in excess of what would be applied to the environment as potassium silicate. Furthermore, no direct application of potassium silicate to birds is expected. It is concluded that when potassium silicate is applied in accordance with accepted labeling, there will be no adverse effects on birds.

Study Protocol	Species	Effects	Toxicity Category	Reference
Studies with soluble Sodium silicate				
Non-guideline	Meleagris gallopavo (male turkey)	4-wk study with 270 ppm sodium silicate in diet reported no adverse effects; pH not reported	No observed toxicological effects	Kayongo- Male & Jia, 1999
Non-guideline	Gallus domesticus (broiler chicken)	16-day study with 250 mg/kg silica had no effect on growth or skeletal development	No observed toxicological effects	Elliot & Edwards, 1991

## b. Freshwater Fish Acute Toxicity

No Guideline studies (OPPTS 850.1075) were submitted. In lieu of Guideline studies, the registrant submitted data from non-EPA guideline studies and OECD guideline studies contained in comprehensive ecological effects reviews for potassium silicates and related soluble silicates [HERA, 2005; IUCLID 1995; NOSB/TAP, 2003 (see Table 2)]. Additional publicly-available literature was reviewed by EPA. Soluble silicates were practically non-toxic to fish with 96-hr LC50s ranging from 146 mg/L for *Leciscus idus* (Golden orfe) to 3185 mg/L for *Brachydanio* rerio (zebra fish). In all studies, toxicity was assumed to have resulted from the effects of high pH rather than from any direct effects of the test substance. Even at a range of pH 7.2-10.1, the test substances were practically non-toxic for the duration of the studies. Most natural aquatic ecosystems fall within the range of pH 6-9 and due to the high buffering capacity of these ecosystems, effects on pH by applied potassium silicate is highly unlikely (HERA, 2005). The presence of soluble silicates in water has been demonstrated to be beneficial to fish by reducing the bioavailability (and toxicity) of soluble aluminum in fish-bearing waters (Birchall et al., 1989; Exley et al., 1997). Naturally-occurring potassium and silica are present at levels in excess of what would be applied to the environment as potassium silicate. Since the end-use product is not intended for use on aquatic sites, exposure to the product is mitigated. Any inadvertent exposure to aquatic sites would not be expected to affect pH because the product is unbuffered. It is concluded that when potassium silicate is applied in accordance with accepted labeling, there will be no adverse effects on fish.

Table 2 Freshwater Fish Studies

Study Protocol	Species	Data (pH)	Toxicity Category	Reference	
Studies with soluble Potassium silicate					
	Leuciscus idus	48-hr LC50 > 146 mg/L		HERA (2005)	
OECD 203:			Practically		

Practically

Study Protocol	Species	Data (pH)	Toxicity Category	Reference
DIN 38412/15	(Golden orfe)	(pH not reported)	non-toxic	
(Germany)]	Leuciscus idus (Golden orfe)	48-hr LC50 > 500 mg/L (pH not reported)		IUCLID (1995)
S	tudies with soluble Sodius	m meta-silicate (ms) or soluble Sod	lium silicate (s)	
ISO 7346/2	Danio rerio (Zebra fish)	96-hr LC50 = 210 mg/L (ms) (pH 9.1-9.8)		HERA (2005)
OECD 203	Danio rerio (Zebra fish)	96-hr LC50 = 1108 mg/L (s) NOEC (mortality) = 348 mg/L (pH 7.9-10.3)		HERA (2005)
	Brachydanio rerio (Zebra fish)	96-hr LC50 = 3185 mg/L (pH 8.0)	Practically	IUCLID (1995)
	Oncorhynchus mykiss (Rainbow trout)	96-hr LC50 = 260 mg/L (s) (pH 6.8-7.5) 96-hr LC50 = 310 mg/L (s) (pH 7.2-8.0)	non-toxic	HERA (2005)
Non-guideline	Gambusia affinis (Mosquito fish)	96-hr LC50 = 2320 mg/L (s) (pH 8.9-10.1)		HERA (2005)
	Lepomis macrochirus (Bluegill sunfish)	96-hr LC50 =301-478 mg/L (pH not reported)		IUCLID (1995)

# c. Aquatic Invertebrate Acute Toxicity

No Guideline studies (OPPTS 850.1010) were submitted. In lieu of Guideline studies, the registrant submitted data from non-EPA guideline studies and OECD guideline studies contained in comprehensive ecological effects reviews for potassium silicates and related soluble silicates (HERA, 2005; IUCLID 1995; NOSB/TAP, 2003). Soluble silicates were practically non-toxic to aquatic invertebrates with 48-hr EC50s ranging from 146 mg/L for *Leciscus idus* (Golden orfe) to 3185 mg/L for *Brachydanio rerio* (zebra fish). In all studies, toxicity was assumed to have resulted from the effects of high pH rather than from any direct effects of the test substance. Although the reported pH of some of the test substances was up to pH 9.8, the test substances were practically non-toxic for the duration of the studies. Naturally-occurring soluble silicates are continuously removed from water by numerous aquatic organisms, such as diatoms, radiolarians, silicoflagellates, and certain sponges which serve as a sink for silica by incorporating it into their shells and skeletons (HERA 2005). Naturally-occurring potassium and silica are present at levels in excess of what would be applied to the environment as potassium silicate. Since the end-use product is not intended for use on aquatic sites exposure to aquatic

organisms to the product is mitigated. Any inadvertent exposure to aquatic sites would not be expected to affect pH because the product is unbuffered. It is concluded that when potassium silicate is applied in accordance with accepted labeling, there will be no adverse effects on aquatic invertebrates.

Table 3. Aquatic Invertebrate Studies.

Study Protocol	Species	Data (pH)	Toxicity Category	Reference	
	Studies with soluble Potassium silicate				
OECD 202; EU Guideline 92/69/EWG	Daphnia magna (Daphnia)	48-hr EC50 > 146 mg/L (pH not reported)	Practically	HERA (2005)	
DIN 38412/11 [Germany]	Daphnia magna (Daphnia)	24-hr EC50 > 500 mg/L (pH not reported)	non-toxic	IUCLID (1995)	
	St	udies with soluble Sodium silicate			
ISO 7346/2	Daphnia magna (Daphnia)	48-hr EC50 = 1700 mg/L (pH 9.1-9.8)		HERA (2005)	
Not reported	Daphnia magna (Daphnia)	96-hr EC50 = 216 mg/L (pH 9.1) Note: static test in lake water		IUCLID (1995)	
Not reported	Daphnia magna (Daphnia)	100-hr EC50 = 247 mg/L (pH not reported)	Practically	IUCLID (1995)	
Not reported	Lymnea spp. (Snail eggs)	48-hr EC50 = 632 mg/L (egg hatching) (pH not reported)	non-toxic	NOSB/TAP (2003)	
Not reported	Hyallela spp. (Amphipods)	96-hr EC50 = 160 mg/L (immobilization) (pH not reported)		NOSB/TAP (2003)	

# d. Non-Target Plant Toxicity

No Guideline studies (OPPTS 850.4100 & 850.4150) were submitted. In lieu of Guideline studies, the registrant submitted data from an OECD guideline study contained in a comprehensive ecological effects review for potassium silicates and related soluble silicates (HERA, 2005). The study demonstrated that a 72-hr EC50 was = 207 mg/L for biomass accumulation in the green algae *S. subspicatus*. Reduced biomass accumulation was attributed to the relatively high pH of the test substance, rather than to any toxicity. Potassium and silica are naturally-occurring and ubiquitous in the soil. Therefore, plants are continually exposed to

potassium and silica compounds. Potassium is present in seeds, seedlings, and mature plants and is an essential nutrient required for growth and health of plants (Mengel and Kirby, 1978). In plants, potassium has an important role in enzyme activation, the opening and closing of stomates, and the maintenance of cellular osmotic balance (Johnson, 2003).

Silica also is ubiquitous in plants and is present primarily as silica gel [hydrated amorphous silica, (Si)O<sub>2</sub>·nH<sub>2</sub>O, or polymerized silicic acid] in the cell walls, and as monosilicic acid in the xylem sap (Mengel and Kirby, 1978). Most soils contain significant quantities of silica, although continuous cropping systems may result in significant removal of silica by plants to the point where silica fertilization is required (NOSB/TAP, 2003). For example, sugarcane may remove up to 380 kg/ha/year from the soil (review by Savant et al., 1999).

Potassium silicate has been recommended for use as a crop fertilizer for a variety of crops (NOSB/TAP, 2003; and Yao et al., 2003). Silica (applied as potassium silicate) has been demonstrated to counteract the toxic effects of excess aluminum, cadmium, and manganese in contaminated soils and hydroponic solutions (Barcelo et al., 1993; Horst and Marschner, 1978; Tredar and Ciesliski, 2005) and to suppress the effects of pathogenic fungi (Cherie et al., 1992; Kant et al., 2004). Silicate fertilizers applied to cucumbers at rates of up to 1400 kg SiO<sub>2</sub>/A/year for three consecutive years were observed to increase growth and reduce wilt disease damage (NOSB/TAP, 2003). There are no reports available regarding any plant toxicity following treatments with potassium, silica, and/or potassium silicate. Naturally-occurring potassium and silica are present at levels in excess of what would be applied to the environment as potassium silicate. It is concluded that when potassium silicate is applied in accordance with approved labeling, there will be no adverse effects on plants.

Table 4. Plant Study

Study Protocol Species		Data (pH)	Toxicity Category	Reference
	Studies w	ith soluble Sodium silicate		
OECD 201; DIN 38412/9 (Germany)] Scenedesmus subspicatus (algae)		72-hr EC50 (biomass) = 207		HERA (2005)

# e. Non-Target Insect Toxicity

A Guideline study (OPPTS 850.3020) conducted by the registrant (MRID 469887-01) demonstrated that the 48-hr LD50 for potassium silicate is >25.6 ug potassium silicate/bee (practically non-toxic). The pH of the test solution was reported as pH 9.99, whereas the CSF for the EP (EPA Reg. No. 82100-1) lists a pH of 11.1. However, it is noted that the EP is unbuffered and will be diluted prior to application, which will lower the pH of the solution to be applied. Therefore, there are no concerns that the pH of the applied product will have any adverse effects on honey bees or other non-target insects when the product is used in accordance with approved labeling.

Table 5. Plant Study

Study Protocol	Species	Data (pH)	Toxicity Category	Reference
	Studies	with Potassium silicate		
OPPTS 850.3020	Apis mellifera (European Honey bee)	48-hr >25.6 ug/L (pH 9.99)	Practically non-toxic	MRID 469887-01

#### 2. Environmental Fate Assessment

When dissolved in water, the active ingredient potassium silicate dissociates into potassium cations, hydroxide anions, and mono- and polysilicic acids. The active ingredient does not contain any volatile organic compounds and will not degrade to any hazardous or environmentally persistent breakdown products (NOSB/TAP, 2003). Dissolved soluble silica from commercial sources will be indistinguishable from dissolved soluble silica from natural sources and any soluble silica input into aquatic or terrestrial environments will be insignificant in relation to the high flux of the natural silica cycle (IUCLID, 1995). The primary hazard to non-target organisms results from the alkaline pH of the active ingredient, potassium silicate, a soluble silicate compound (HERA, 2005; IUCLID, 1995). The end-use product (AgSil®25; EPA Reg. No. 81200-1) is approximately pH 11.1, but it is unbuffered. Therefore, when applied to terrestrial and aquatic environments, commercial potassium silicate formulations will have little effect on pH due to the high buffering capacity of the natural environments (HERA, 2005). At environmental pH [approximately pH 4.5-9; (Smith, 2001)], potassium cations are readily soluble, but soil solution concentration is dependent upon clay content and clay type (Mengel and Kirby, 1978). Below pH 9, soluble silicates are present as poorly soluble amorphous silica and monosilicic acid (HERA, 2005).

The need for environmental fate and groundwater data (Tier II, (40 CFR Section 158.690(d)(2)(vii through xv)) was not triggered because the Tier I studies were waived. Risk is minimal due to low toxicity, use pattern, and application methods.

# 3. Ecological Exposure and Risk Characterization

#### a. Environmental Exposure Assessment

Worldwide production of soluble silicates (sodium silicate, disodium metasilicate, and potassium silicate) is approximately 3-4 million metric tons per year (HERA, 2005). Soluble silicate exposure (from commercial sources) to aquatic and terrestrial environments occurs via uses in detergents, pulp and paper effluent, water/wastewater treatment, soil stabilization, and as fertilizer (HERA, 2005; NOSB/TAP, 2003; Perry & Keeling-Tucker, 2000). When used as a fertilizer, potassium silicate is used primarily as a silica amendment (NOSB/TAP, 2003). Due to their ubiquitous distribution in terrestrial and aquatic environments, non-target organisms are continually exposed to soluble silicates (including potassium silicate), potassium, silicon dioxide, and silica gel via contact and/or oral exposure.

# b. Naturally-Occurring Potassium and Silicon

#### i. Potassium

Potassium is a common basic cation found in the environment and is an essential element in human and plant nutrition (Johnson, 2003). In plants, potassium has an important role in enzyme activation and the maintenance of cellular osmotic balance; as in plants, potassium is necessary in animals for maintaining osmotic equilibrium as well as participating in life-supporting activities such as nerve impulses, heartbeat, and enzyme activation (Johnson, 2003). Potassium is a common soil plant nutrient and fertilizer (as  $K_2O$ ). Potassium comprises approximately 2.59% of the Earth's crust by weight (Merck, 1983). The primary source of naturally-occurring soluble potassium is from the weathering of potassium containing minerals [e.g. alkali feldspars; (Mengel and Kirby, 1978)]. Mobility of potassium in the soil is dependent upon the clay content, the type of clay (vermiculite, illite, montmorillonite, or kaolinite), and to a lesser extent, pH; potassium content is higher in high clay content soil and is greater with 2:1 clays (e.g. montmorillonite) than in 1:1 clays [e.g. kaolinite (Mengel and Kirby, 1978)].

#### ii. Silicon

Silicon also is ubiquitous in the environment, comprises approximately 32% of the soil by weight (review by Savant et al., 1999) and is present as dissolved silica, amorphous silica in the solid phase, and silica bound to organic matter (IUCLID, 1995). Silicon is the second most

abundant element in the lithosphere after oxygen (Mengel and Kirby, 1978). At less than pH 9, Si is present in soil solution primarily as monosilicic acid (Si(OH)<sub>4</sub> and as silicate ions at higher pH (Mengel and Kirby, 1978). The solubility of silica is relatively constant in a pH range between 2 to 8.5, and increases rapidly above pH 9 (review by Savant et al., 1999). The pHdependent adsorption on sequioxides (e.g. iron oxide, aluminum oxide) controls the concentration of silicic acids in soil solution, which decreases on either side of a maximum at pH 9.5 (Mengel and Kirby, 1978); adsorption is greatest on aluminum oxides. In the normal range of soil pH, silicic acid is the major silicate in soil water (IUCLID, 1995). In natural waters most dissolved silica results from the weathering of silicate minerals. It is estimated that silica is introduced into the environment via weathering at a rate of approximately 2000 kg/square km/year and natural waters may contain 3.8-363 ppm soluble silica (IUCLID, 1995) depending on the geological materials with which the waters are in equilibrium. The high and variable flux of the natural silica cycle will cause influx of soluble silicates from commercial sources to be insignificant in relation to silica from natural sources (IUCLID, 1995). According to a review by HERA (2005), "silica is continuously removed from water by biochemical processes: diatoms, radiolarians, silicoflagellates, and certain sponges serve as a sink for silica by incorporating it into their shells and skeletons as amorphous biogenic silica, frequently referred to as opal (SiO<sub>2</sub>·nH<sub>2</sub>O)." Commercial soluble silicates rapidly degrade to molecular forms that are indistinguishable from natural dissolved silica (IUCLID, 1995). The most common form of silica, quartz, comprises approximately 12% of the Earth's crust (IARC, 1997) by volume. Beach sand is almost 100% silica (Crop Protection handbook, 2003). Silica is chemically unreactive. Silica and silica gel (a hydrated amorphous form of silica) are considered GRAS by FDA (21 CFR 182.90 and 21 CFR 182.1711).

When used as a pesticide, potassium silicate residues are low relative to naturally present concentrations and other uses in the environment. Minimal potential for additional exposure exists to insects, fish and other nontarget wildlife as a result of potassium silicate use as a pesticide.

#### D. EFFICACY DATA

No efficacy data are required, because no public health uses are involved.

# IV. Risk Management Decision

#### A. DETERMINATION OF ELIGIBILITY FOR REGISTRATION

Section 3(c)(5) of FIFRA provides for the registration of new active ingredients if it is determined that (A) its composition is such as to warrant the proposed claims for it; (B) its labeling and other materials required to be submitted comply with the requirements of FIFRA; (C) it will perform its intended function without unreasonable adverse effects on the

environment and (D) when used in accordance with widespread and commonly recognized practice it will not generally cause unreasonable adverse effects on the environment.

To satisfy criterion (A) above, potassium silicate will protect agricultural commodities from fungi, insects and mites. Criterion (B) is satisfied by the current label and by the data presented in this document. It is believed this new pesticidal active ingredient will not cause any unreasonable adverse effects, satisfying Criterion (C). Criterion (D) is satisfied by the data submitted and the low exposure to the product when used according to the label's directions.

Therefore, potassium silicate is eligible for registration. The uses are listed in Table 4, Appendix A.

#### **B. REGULATORY POSITION**

#### 1. Unconditional Registration

All data requirements have been fulfilled and/or waived by the Agency and the Biopesticides and Pollution Prevention Division approved unconditional registration of products which contain potassium silicate as their sole active ingredient.

# 2. Exemption from the Requirement of a Tolerance for food uses

EPA received a pesticide petition proposing, pursuant to section 408(b)(2)(D) of the Federal Food, Drug and Cosmetic Act, 21 U.S.C. section 346, to amend 40 CFR Part 180 by establishing an exemption from the requirement of a tolerance for the pesticide ingredient, potassium silicate. This was granted June 14, 2006 (71 FR 34272), 40 CFR 180.1268 so long as potassium silicate is not applied at rates greater than 1.0% by weight in aqueous solutions.

#### 3. CODEX Harmonization

There is no CODEX or international tolerance exemption established for the subject active ingredient at this time.

# 4. Nonfood Re/Registrations

There are no non-food issues at this time. The non-food uses are listed in Appendix A, Table 4.

#### 5. Risk Mitigation

There are no significant risk issues. Risks to workers are mitigated by protective clothing requirements and a 4-hour re-entry interval restriction.

# 6. Endangered Species Statement

EPA concludes that potassium silicate does not pose an unreasonable risk to the environment, including non-target organisms, when used according to label directions. The primary hazard resulting from use of potassium silicate is its high pH (approximately 11.1). However, since most terrestrial and aquatic ecosystems are highly buffered in the slightly acid to slightly alkaline range (pH 5-9), and end-use products will be diluted prior to use, application of the unbuffered potassium silicate will have little effect on environmental pH and non-target organisms. Therefore, when used in accordance with accepted labeling, use of potassium silicate products will have No Effects (NE) on endangered species.

#### C. LABELING RATIONALE

It is the Agency's position that the labeling of the end use and the technical grade active ingredient products containing, respectively, 29.1% and 99.40% potassium silicate complies with current pesticide labeling requirements.

#### 1. Human Health Hazard

### a. Worker Protection Standard

This product comes under the provisions of the Worker Protection Standard (WPS). PPE (long-sleeved shirt and long pants, socks, shoes, and gloves) and REI (4-hour) required.

#### b. Non-Worker Protection Standard

There are no non-WPS human health hazard issues.

### c. Precautionary Labeling

The Agency has examined the toxicological data base for potassium silicate products and concluded proposed precautionary labeling (i.e., Signal Word, Statement of Practical Treatment and other label statements) adequately mitigates any risks associated with the proposed uses.

**Technical Product Precautionary Labeling:** For potassium silicate is "CAUTION."

Hazards to Humans and Domestic Animals:

Harmful if swallowed. Causes moderate eye irritation. Avoid contact with eyes or clothing. Wash thoroughly with soap and water after handling and before eating, drinking, chewing gum, or using tobacco. Remove and wash contaminated clothing before reuse. Wear: Long-sleeved shirt and long pants, socks, shoes, and gloves.

#### First Aid:

#### If swallowed:

- -Call a poison control center or doctor for treatment advice.
- -Have person sip a glass of water if able to swallow.
- -Do not induce vomiting unless told to do so by a poison control center or doctor.
- -Do not give anything to an unconscious person.

# If on skin or clothing:

- -Take off contaminated clothing.
- -Rinse skin immediately with plenty of water for 15-20 minutes.
- -Call a poison control center or doctor for treatment advice.

# If in eyes:

- -Hold eye open and rinse slowly and gently with water for 15-20 minutes.
- -Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye.
- -Call a poison control center or doctor for treatment advice.

**End-Use product Precautionary Labeling:** For end use potassium silicate is "CAUTION."

#### Hazards to Humans and Domestic Animals:

Causes moderate eye irritation. Avoid contact with eyes or clothing. Wash thoroughly with soap and water after handling and before eating, drinking, chewing gum, or using tobacco. Remove and wash contaminated clothing before reuse. Wear: Long-sleeved shirt and long pants, socks, shoes, and gloves.

#### First Aid:

If in eyes:

- -Hold eye open and rinse slowly and gently with water for 15-20 minutes.
- -Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye.
- -Call a poison control center or doctor for treatment advice.

#### 2. Environmental Hazards Labeling

**End-Use Product Environmental Hazards Labeling:** Potassium silicate is considered nontoxic to the environment and no environmental hazard statement is required on the end-use product's label.

# 3. Application Rate

It is the Agency's position that the labeling for the end-use pesticide product containing potassium silicate complies with current pesticide labeling requirements.

#### D. LABELING

(1) Product name: **Technical Potassium Silicate** 

Active Ingredient:	
Potassium Silicate	99.4%
Other Ingredients	0.6%
Total	100.0%
Product name: AgSil®25	
Product name: <b>AgSil®25</b> Active Ingredient:	
Product name: <b>AgSil®25</b> Active Ingredient: Potassium Silicate	29.1%

Signal word is "CAUTION".

The product shall contain the following information:

- Product Name
- Ingredient Statement
- Registration Number
- Signal Word (CAUTION)

# V. Actions Required by Registrants

There are no data requirements, label changes or other responses necessary for the reregistration of the end-use product since the product is being registered after November 1984 and is, therefore, not subject to reregistration. There are also no existing stocks provisions at this time.

# VI. Appendix A

Table 4 lists the use sites for the product.

Table 4. Use Site Registration

Technical Potassium Silicate (99.4% potassium silicate)	Official date registered:
<u>Use sites</u> : Manufacturing use product	May 11, 2006
AgSil®25 (29.1% potassium silicate)	Official date registered:
<u>Use Sites</u> : agricultural crops, fruits, nuts, vines, turf and ornamentals	May 11, 2006

#### VII. References

- 1. Anderson, J., L. Young, and E. Long. 2005. Potassium and health. Colorado State Cooperative Extension Nutrition Resources No. 9.355. <a href="https://www.ext.colostate.edu/pubs/foodnut/09355.html">www.ext.colostate.edu/pubs/foodnut/09355.html</a>
- 2. Barcelo, J., P. Guevara, and C. Poschenrieder. 1993. Silicon amelioration of aluminum toxicity in teosinte (*Zea mays* L. ssp. mexican). Plant and Soil 154(2): 249-255.
- 3. Chao, H. M. Letter from FDA GRAS Review Branch to W. L. Schleyer (PQ Corporation), dated 8 June 1978.
- 4. Cherie, M., N. Benhamou, J. G. Menzies, and R. R. Belanger. Silicon induced resistance in cucumber plants against *Pythium ultimum*. Physiological and Molecular Plant Pathology 6: 411-425.
- 5. Elliot, M. A. and H. M. Edwards. 1991. Effect of dietary silicon on growth and skeletal development in chickens. Journal of Nutrition 121(2): 201-207.
- 6. Exley, C., J. K. Pinnegar, and H. Taylor. 1997. Hydroxyaluminosilicates and acute aluminum toxicity in fish. Journal of Theoretical Biology 189: 133-139.

- 7. Horst, W. J., and H. Marschner. 1978. Effects of silicon on manganese tolerance of bean plants (*Phaseolus vulgaris* L.). Plant and Soil 50(1): 287-303.
- 8. Human Environmental Risk Assessment (HERA) On Ingredients of European Household Cleaning Products. Soluble Silicates (Draft), pp. 17-28. February 2005.
- 9. International Agency for Research on Cancer (IARC), World Health Organization. 1997. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, 1972-Present. p. V68: 59.
- 10. International Uniform Chemical Information Database (IUCLID). Potassium/Sodium Silicate. January 1995.
- 11. Johnson, A. E. 2003. Understanding Potassium and Its Use in Agriculture. European Fertilizer Manufacturers Association.
- 12. Kant, T., A. Miyoshi, T. Ogawa, K. Maekawa, and M. Aino. 2003. Suppressive effect of potassium silicate on powdery mildew of strawberry in hydroponics. Journal of General Plant Pathology 70(4): 207-211.
- 13. Mallarino, A. and J. E. Sawyer. 2003. Use new potassium soil test and fertilizer recommendations. Integrated Crop Management. General Guide for Crop Nutrient and Limestone Recommendations in Iowa. PM 1688. <a href="https://www.extension.iastate.edu/pubs">www.extension.iastate.edu/pubs</a>
- 14. Mengel, K. and Kirby, E.A. 1982. Principles of Plant Nutrition. Publication of the International Potash Institute, Berne, Switzerland.
- 15. Merck Index, 10th Ed. 1983. The Merck Company, Inc., Rahway, NJ. p. 1098
- 16. National Organic Standards Board/Technical Advisory Panel (NOSB/TAP). 2003. Potassium Silicate for Use in Crop Production. Compiled by the University of California Sustainable Agriculture Research and Education Program (UC SAREP) for the National Organic Program. September 2003.
- 17. Nielsen, F. H. 1991. Nutritional requirements for boron, silicon, vanadium, nickel, and arsenic: current knowledge and speculation. FASEB Journal 5: 2661-2667.
- 18. Perry, C. C., and T. Keeling-Tucker. 2000. Biosilification: The role of the Organic Matrix in Structure Control. Journal of Biological Inorganic Chemistry 5(5): 537-550.

- 19. Savant, N. K., G. H. Korndorfer, L. E. Datnoff, and G. H. Synder. 1999. Silicon Nutrition and Sugarcane Production: A Review. Journal of Plant Nutrition 22(12)1853-1903.
- 20. Smith, T. 2001. Some Thoughts About Soil pH, Fertilizer, and Lime. Washington State University Extension, Wenatchee & North. www.ncw.wsu.edu/treefruit/soil/lime.htm
- 21. USDA/ERS. 2002. Agricultural chemicals and production technology: Questions and answers. www.ers.usda.gov/Briefing/AgChemicals/Questions/nmqa3.htm
- 22. USEPA/OPP. Silicon Dioxide and Silica Gel Registration Eligibility Document (RED). 738-F-91-107, September 1991.
- 23. Yao, Y., T. Yoneyama, and H. Hayashi. 2003. Potassium uptake by Chinese cabbage (*Brassica pekinensis* Rupy.) from fused potassium silicate, a slow-releasing fertilizer. Plant and Soil 249(2): 279-286.

# Phosphorous acid and its ammonium, sodium, and potassium salts (076002) Mono- and dipotassium salts of phosphorous acid (076416) Fact Sheet

# **Summary**

The ammonium, potassium, and sodium salts of phosphorous acid are used primarily for controlling downy mildew and brown rot, harmful fungi that attack a variety of food and non-food crops. In addition to controlling the fungi directly, these active ingredients appear to enhance the plant's natural defense mechanisms. No harm to humans or the environment is expected when users follow label directions.

# I. Description of the Active Ingredient

**Name of Active Ingredient:** Mono- and di-potassium salts of phosphorous acid OPP Chemical Code: 076416 [CAS # 13977-65-6 (mono-K); 13492-26-7 (di-K)]

**Name of Active Ingredient:** Phosphorous acid and its ammonium, sodium, and potassium salts OPP Chemical Code: 76002

Phosphorous acid and its salts are not found naturally, but are closely related to common substances that are found throughout the environment. The active ingredients are directly toxic to the target fungi, and also appear to increase the effectiveness of the plants' defense mechanisms.

#### II. Use Sites, Target Pests, and Application Methods

- **Use sites:** Many food and non-food crops, including turf, ornamentals, trees. Can be used outdoors and indoors, e.g., nurseries, greenhouses, parks, golf courses).
- o **Target pests:** Various fungi including Phytophthora and Pythium
- Application methods: Products are applied before any disease develops, and at subsequent intervals of 2 to 3 weeks. Can be applied by spraying leaves, using sprinkler irrigation systems, direct addition to soil, and dipping roots for transplant.

#### III. Assessing Risks to Human Health

Whether or not a substance poses a risk to humans or other organisms depends on two factors: how toxic the substance is, and how much of it an organism is exposed to. Therefore, the EPA considers both toxicity and exposure data in determining whether to approve a pesticide for use Based on tests with animals, these chemicals are not expected to harm humans. The substances have been used in Australia and other countries for more than ten years with no indication of adverse effects.

# IV. Assessing Risks to the Environment

Studies show that the active ingredients are not harmful to most non-target organisms, but are somewhat toxic to fish and aquatic invertebrates. To protect aquatic species, product labels instruct users not to apply the pesticide product to water and not to contaminate water during disposal.

# V. Regulatory Information

Products with these active ingredients were registered (licensed for sale) in November 1997 (OPP ID # 76416), and in October 2000 (OPP ID # 76002). In April 2001, there were three registered end-use products containing salts of phosphorous acid as active ingredients.

#### VI. Producer Information

Three companies have registered products containing the above active ingredients.

#### VII. Additional Contact Information

Ombudsman, Biopesticides and Pollution Prevention Division (7511P)
Office of Pesticide Programs
Environmental Protection Agency
1200 Pennsylvania Avenue, NW
Washington, D.C. 20460